Title: SELF ASSEMBLING NANOPARTICLE-POLYMER HYBRIDS

Abstract: A nanoparticle-polymer hybrid having a nanoparticle including a surface having a polymer grafted portion and a polymer incompatible portion. At least one polymer chain is grafted to the outer surface of the nanoparticle at the polymer grafted portion. The at least one polymer chain and polymer incompatible portion of the nanoparticle interact causing self assembly of the nanoparticle-polymer hybrid into an ordered material.

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SELF ASSEMBLING NANOPARTICLE-POLYMER HYBRIDS

REFERENCE TO RELATED APPLICATIONS

This application claims priority of U.S. Provisional Patent Application Serial No. 60/509,141 filed October 6, 2003, which is incorporated herein by reference.

FIELD OF THE INVENTION

The invention relates to nanoparticle-polymer hybrids, and more particularly to self assembling nanoparticle-polymer hybrids.

BACKGROUND OF THE INVENTION

Nanoparticle-polymer hybrids may be utilized to form various ordered composite materials. Specifically, such composite materials have utility as photonic band gap materials, that is, materials that can control the propagation of electromagnetic radiation by creating periodic dielectric structures. A photonic band gap material is one that prohibits the propagation of electromagnetic radiation within a specified frequency range (band) in certain directions. That is, band gap materials prevent light from propagating in certain directions with specified energies. The band gap properties result in the complete reflection of electromagnetic radiation of a particular frequency directed at the material in at least one direction because of the particular structural arrangement of separate domains of the material, and refractive indices of those domains. The structural arrangement and refractive indices of separate domains that make up these materials form photonic band gaps that inhibit the propagation of light centered around a particular frequency.

Preparation of polymer-based photonic bandgap materials demands composite materials in which high refractive index inorganic nanoparticles are combined with polymers. Polymers have refractive indices between 1.3-1.7 while inorganic semiconductors range from 2-5.
Grafting polymer to nanoparticles is well known. For example, in von Werne, T. and T.E. Patten, *Preparation of Structurally Well-Defined Polymer-Nanoparticle Hybrids with Controlled/Living Radical Polymerizations*. J. Am. Chem. Soc., 1999. **121**: p. 7409-7410, the authors report the synthesis of structurally well-defined polymer nanoparticle hybrids through integrating colloid and nanoparticle syntheses with recently reported controlled/living radical polymerizations. The particles were completely covered with polymer and therefore cannot self-assemble.

Another example is in Mirkin, C.A. and T.A. Taton, *Semiconductors meet biology*. Nature, 2000. **405**: p. 626-627. The paper reports the assembly of inorganic nanoparticles into periodic macroscopic structures by exploiting the simple base-pairing interactions of DNA. This example represents self-assembly, but it is driven by selective interactions between DNA base-pairs, not by phobic interactions between the blocks. In effect, this work uses the self-assembly of DNA as a template to build a structure consisting of particles. The particles participate because they are attached to the DNA chains, but they do not contribute to the self-assembly by any property of their own.

Diblock copolymer – nanoparticle blends have been shown to have photonic band gap properties. For example, U.S. Patent No. 6, 433, 931 discloses mechanical blends of nanoparticles and block copolymers. The microstructure is formed by the block copolymers alone. The nanoparticles are surface treated to selectively incorporate into one of the two blocks, leading to an increase in the refractive index contrast between the two domains. The nanoparticles do not contribute to the self-assembly.

refractive index of about 1.4. Self-assembly of the copolymer system (that is, segregation of the system into polyethylene rich domains and POSS rich domains) is driven by the tendency of polyethylene to crystallize not by surface energy interactions between the POSS nanoparticles and the polymer. The system does not form microstructures with long-range order such as the lamellar, hexagonal, and cubic structures formed by block copolymers. Rather the system forms a disordered segregated structure, similar to the behavior of an oil/water microemulsion. Such disordered systems would not be useful as photonic bandgap materials.

Photonic bandgap materials can serve a variety of useful purposes. Dielectric mirrors, for example, have been known for many years. The ability to engineer microstructures, especially preparation of complex 2D and 3D structures, allows many other possibilities. For example, point defects within a 3D structure could define low loss optical resonance cavities, planar defects could define narrow-band filters, and linear defects within 3D photonic band gap materials could define lossless waveguides capable of guiding light around sharp corners, crucial to the creation of proposed optical computers. Totally-reflective UV or laser shields, and countless other commercial applications would benefit from relatively simple and reliable techniques for forming these materials. There is therefore; a need for creating self assembling nanoparticle-polymer hybrids for use as photonic bandgap materials that are economically practical, easy to manufacture and have the ability to be easily controlled and modified for use in a variety of applications.

SUMMARY OF THE INVENTION

A nanoparticle-polymer hybrid having a nanoparticle including a surface having a polymer grafted portion and a polymer incompatible portion. At least one polymer chain is grafted to the outer surface of the nanoparticle at the polymer grafted portion. The at least one polymer chain and polymer incompatible portion of the nanoparticle interact causing self assembly of the nanoparticle-polymer hybrid into an ordered material.
BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a density contour plot of the spherical nanoparticle and the coil-like polymer of the nanoparticle-polymer hybrid of the present invention;

Figure 2 is a one-dimensional density plot comparing the nanoparticle polymer hybrid shown in 2a with a diblock polymer shown in 2b;

Figure 3 is a density profile of a nanoparticle polymer hybrid having a diblock polymer portion;

Figure 4 is a graphical representation of the nano-particle polymer hybrid of the present invention.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

This invention relates to a nanoparticle-polymer hybrid material suitable for use in creating a self assembling composite material. The nanoparticle-polymer hybrid comprises a nanoparticle including an outer surface having a polymer grafted portion and a polymer incompatible portion and a polymer grafted to the nanoparticle at the polymer grafted portion.

Referring to figure 4, there is shown a graphical representation of the nanoparticle-polymer hybrid 5 of the present invention. The nanoparticle 7 has a polymer grafted 10 region and polymer incompatible region 20. The regions may be defined by using surface coatings to repel the polymer chains 30, which will be discussed in more detail below. The term polymer incompatible may be defined by the equation X*N>10 where X is the Flory-Higgins interaction parameter and N is the degree of polymerization. Alternatively, incompatible may be defined in terms of the surface chemistry of wetting and de-wetting. Incompatible as the term is used in the specification means the polymer chains do not wet the surface of the particle. As can be seen in figure 4, the nanoparticle-polymer hybrid 5 resembles the shape of a tadpole with the nanoparticle 7 representing the head and the polymer chains 30 representing the tail of the tadpole.

The nanoparticle is a rigid, volume excluding, non swellable entity, as opposed to the polymer chain which is swellable and interpenetrating. In a
preferred aspect of the invention the nanoparticle comprises metal oxide particles, semiconductor particles and metal particles. Examples include: SiO₂, TiO₂, PbS, PbSe, PbTe, CdS, CdSe, GaP, GaAs, InP, InAs, InSb, Si both amorphous and crystalline, Ga both amorphous and crystalline, Au, Ag, Ni, Cu, Fe, ZnS, Iron oxide, FeS, rare earth metal garnets, such as Tb₃Fe₅O₁₂ and Y₃Fe₅O₁₂ (Ytrrium Iron Garnet YIG) and Bismuth and Cerium doped YIG, as well as other magnetic particles that can be utilized to tune the structure of the nanoparticle-polymer hybrid, which are not limiting, rather the nanoparticle may comprise any material that is capable of having a chemical species covalently bonded to its surface, and possess the necessary physical properties for its intended use. In a preferred aspect of the present invention the nanoparticle has a size of from 3 to 100 nanometers and even more preferably from 20 to 25 nanometers.

In a preferred aspect of the present invention, the nanoparticle is treated with a coating material to form the polymer grafted and polymer incompatible regions of the nanoparticle. The coating of the polymer incompatible portion may comprise alkyl thiols, silanes, hydrocarbons and small chain silicones. The silanes are preferably of the structure X₃R₆R₂R₄Si, whereby a is a hydrolysable moiety chosen from halogens, preferably chloride, bromide or iodide and more preferable chloride, a hydrolysable moiety chosen from alkoxy, alcohol, esters and amines bearing a hydrogen atom or bearing hydrocarbon radicals with homo atom or hetero atom chains ranging from 1 to 20, preferably 1-8 and more preferably 1-6 and even more preferably 1-4 including by not limited to methyl, methoxy, acetoxy, ethyl, ethoxy, propyl, propoxy, isopropyl, isopropanoxy, butyl, iso-butyl, t-butyl, butoxy, iso-butoxy, t-butoxy and phenyl. The range for a can be from 1 to 3, preferably 1. R can be chosen from hydrocarbon radicals with homo atom or hetero atom chains ranges from 1-100, preferable 1-30 and more preferable 1-18, and even more preferable 1-6 including alkyl, aryl, alkaryl, alkalkyl, alkylether, arylether, alkakylether, alkylether, alkylester, arylester, alkalkylester, alkalkylester, aklyamino, arylamino, alkalkylamino, alkarylamino, and more specifically
include methyl, ethyl, propyl, iso-propyl, butyl, iso-butyl, t-butyl, pentyl and phenyl with the total of $a + b + c + d$ equaling 4, preferable with $b + c + d$ equal to or less than 3. Examples of hydrophobing silanes include:

Acetoxyethyltrimethylchlorosilane, Acetoxyethylmethylidichlorosilane,
Acetoxyethyltrichlorosilane, Acetoxyethyltrimethyldichlorosilane,
Acetoxypropylmethylidichlorosilane, Acetoxypropyltrimethyldichlorosilane,
Benzyltrimethylchlorosilane, Benzyltrichlorosilane, Benzyltrimethyldichlorosilane,
Bis(methylidichlorosilyl)butane, Bis(methylidichlorosilyl)ethane, 1,2-
Bis(trichlorosilyl)ethane, 1,8-Bis(trichlorosilyl)hexane, 1,9-
Bis(trimethyldichlorosilyl)nonane, Bis(3-trimethyldichlorosilyl)hexane, Bis[3-
(trimethyldichlorosilyl)propyl]ethylenediamine, 1,3-Bis(trimethylsiloxyl)-1,3-
dimethylsiloxane, n-Butylationdichlorosilane, n-Butyltrichlorosilane, t-
Butyltrichlorosilane, 10-(Carboxethoxy)decyldimethylchlorosilane, 2-
(Carboxethoxy)ethylmethylidichlorosilane, 2-
(Carboxethoxy)ethyltrimethyldichlorosilane, 2-
(Carboxethoxy)ethyltrichlorosilane, Carboxyethylsilanetriol Sodium Salt, 3-
Chloropropylmethylidichlorosilane, 3-Chloropropyltrimethyldichlorosilane, 3-
Chloropropyltrichlorosilane, Chloropropyltrimethyldichlorosilane, 3-
Cyanopropyldiisopropylchlorosilane, 3-
Cyanopropyltrimethyldichlorosilane, 3-Cyanopropyltrimethylchlorosilane, 3-
Cyanopropyltrichlorosilane, 3-Cyanopropyltrimethyldichlorosilane, n-
Decylidichlorosilane, n-Decyltrichlorosilane, n-Decyltrimethyldichlorosilane,
Di-
Butylidichlorosilane, Diphenylmethylidichlorosilane,
Diphenylmethoxyisilane, Diphenylidichlorosilane Diphenylidethoxysilane,
1,7-Dichlorooctamethyltetrasiloxane, 1,5-Dichlorohexamethyltrisiloxane, 1,3-
Dichlorotetramethyldisiloxane, (N,N-Dimethyl-3-
aminopropyl)trimethyldichlorosilane, Dimethyldichlorosilane,

Dimethyldimethoxysilane, Dimethyldimethoxysilane, 3-(2,4-
Dinitrophenylamino)propyl-trimethoxysilane, Di-n-Octyldichlorosilane,
Diphenyl dichlorosilane, Diphenyl diethoxysilane, Diphenyl diethoxysilane, 2-(3,4-Epoxycyclohexylethyl)trimethoxysilane, Ethyl dimethylchlorosilane, Ethyl methyl dichlorosilane, Ethyltrichlorosilane, Ethyltriethoxysilane, Ethyltrimethoxysilane, 3-Glycidoxypropyl)triethoxysilane, (3-Glycidoxypropyl)trimethoxysilane, (Heptadecafluoro-1,1,2,2-Tetrahydrodecyl)dimethylchlorosilane, (Heptadecafluoro-1,1,2,2-Tetrahydrodecyl)trichlorosilane, (Heptadecafluoro-1,1,2,2-Tetrahydrodecyl)triethoxysilane, (Heptadecafluoro-1,1,2,2-Tetrahydrodecyl)methyl dichlorosilane, (3Heptafluorooisopropoxy)propyltrichlorosilane, n-Heptyldimethylchlorosilane, n-Heptylmethyl dichlorosilane, n-Heptyltrichlorosilane, n-Hexamethyltrichlorosilane, Hexamethyl disilazane, Hexylmethyl dichlorosilane, Hexyltrichlorosilane, Hexyltriethoxysilane, 2-Hydroxy-4-(3-triethoxysilylpropoxy)-diphenyl ketone, Isobutyl dimethylchlorosilane, Isobutyl trichlorosilane, Isobutyltriethoxysilane, Isobutyltrimethoxysilane, 3-Isocyanatopropyltriethoxysilane, Isopropyl dimethylchlorosilane, Isopropyl methyl dichlorosilane, Mercapto methyl dimethyldiethoxysilane, Mercapto propyl methyl dimethoxysilane, 3-Mercapto propyltriethoxysilane, Mercapto propyl trimethoxysilane, 3-Mercapto propyl trimethoxysilane, Methacryloxypropyltrichlorosilane, Methacryloxypropyltriethoxysilane, Methacryloxypropyl trimethoxysilane, 3-(p-Methoxy phenyl) propyltrichlorosilane, 3-Methoxypropyltrimethoxysilane, Methyl trichlorosilane, Methyl triethoxysilane, Methyl trimethoxysilane, n-Octade clyl diisobutyldimethylamine silane, n-Octadecyldimethylchlorosilane, n-Octadecyldimethyl(dimethy lamino) silane, n-Octadecyldimethylmethoxysilane, n-Octadecyldimethyl(3-trimethoxysilylpropyl) ammonium chloride, n-Octadecyldimethyl dichlorosilane, n-Octadecyldimethyl diethoxysilane, n-Octadecyl trichlorosilane, n-Octadecyl triethoxysilane, n-Octadecyl trimethoxysilane, n-Octyldiisobutyl chlorosilane, n-Octyl diisopropyl chlorosilane, n-
Octyldiisopropyl(dimethlamino)silane, n-Octyldimethylchlorosilane, n-Octyldimethylmethoxyasilane, n-Octyldimethyl(dimethlaminosilane, n-Octylethyldichlorosilane, n-Octyldimethyl(diethoxy)silane, n-Octyltrichlorosilane, n-Octyltrioethyoxysilane, n-Octyltrimethoxysilane, n-Octyldiisopropylchlorosilane, Pentafluorophenyl(dimethylvchlorosilane, Pentafluorophenylpropyl(dimethylchlorosilane, Pentafluorophenylpropyl(trichlorosilane, Pentafluorophenylpropyl(trimethoxy)silane, Pentyltrichlorosilane, Pentyltrioethyoxysilane, Phenethyl(diisopropylchlorosilane, Phenethyl(dimethylchlorosilane, Phenethyl(dimethyl(dimethlamino)silane, Phenethyltrichlorosilane, Phenethyltrimethoxysilane, 3-Phenoxypropyl(dimethylchlorosilane, 3-Phenoxypropyl(trichlorosilane, Phenyl(dimethylchlorosilane, Phenylethyl(dimethylchlorosilane, Phenylethylmethoxy)silane, Phenylethylmethoxysilane, Phenylpropyl(dimethylchlorosilane, Phenylpropylmethyldichlorosilane, Phenyltrichlorosilane, Phenyltrimethoxysilane, n-Propyl(dimethylchlorosilane, n-Propylmethyldichlorosilane, n-Propyltrichlorosilane, n-Propyltrimethoxysilane, Tetrachlorosilane, Tetraethoxysilane, 2,2,5,5-Tetramethyl-2,5-disila-1-aza-cyclopentane, Trianteyldimethylchlorosilane, Trianteyltrimethoxysilane, (Triocafluoruro-1,1,2,2-tetrahydrooctyl)dimethylchlorosilane, (Triocafluoruro-1,1,2,2-tetrahydrooctyl)methyl(dichlorosilane, (Triocafluoruro-1,1,2,2-tetrahydrooctyl)trichlorosilane, (Triocafluoruro-1,1,2,2-tetrahydrooctyl)trioethyoxysilane, Triethoxysilylpropylethylcarbamate, N-(3-riethoxysilylpropyl)gluconamide, N-(3-Triethoxysilylpropyl)-4-hydroxybutyramide, N-(Triethoxysilylpropyl)-O-polyethylene oxide, 3-(Triethoxysilylpropyl)succinic anhydride, Triethylacetoxysilane, Triethylchlorosilane, (3,3,3-Trifluoropropyl)methyl(dichlorosilane, (3,3,3-Trifluoropropyl)trimethoxysilane, (3,3,3-Trifluoropropyl)trimethoxysilane, 2-(Trimethoxysilyl)ethyl)pyridine,
Trimethylchlorosilane, Trimethyleneoxysilane, Trimethylmethoxysilane, Tri-n-propylchlorosilane, Undecyltrichlorosilane, Ureidopropyltriethoxysilane, Ureidopropyltrimethoxysilane, Vinylmethylidichlorosilane, Vinylmethylidioethoxysilane, Vinylmethylidimethoxysilane, Vinyltrichlorosilane, Vinyltrimethoxysilane, and Vinyltrimethoxysilane.

The coating is preferably applied only on a portion of the nanoparticle comprising less than 70% and greater than 30% of the total surface area. In this manner the novel “tadpole” structure of the nanoparticle-polymer hybrid is achieved, having polymer chains grafted on only one side of the nanoparticle.

The nanoparticle-polymer hybrid of the present invention includes a polymer chain grafted to the polymer grafted portion of the nanoparticle. A non-limiting list of polymeric or block copolymeric species can include those that are defined by or contain blocks of polystyrene, polybutadiene, polyisoprene, polycaprolactone, polyethyleneoxide, poly 2-vinyl pyridene, polydimethyl siloxane, biopolymers including proteins, carbohydrates, and sugars and the like. A vast array of different block copolymers, combinations of different homopolymeric species, or combinations of block copolymeric and homopolymeric species can be used in accordance with the invention, so long as other criteria described herein are met. Polymers and block copolymers may include a wide variety of side chains that can be utilized to alter refractive index, segregated polymer domain size, or cross-link or modify other properties of the nanoparticle-polymer hybrid. Any polymer with the necessary properties for self-assembly of the nano-particle-polymer hybrid requiring two components that are immiscible and separate into two separate domains can be utilized by the present invention.

The microstructure of the nanoparticle-polymer hybrid is determined by the volume fraction of the polymer in relation to the nanoparticle and the surface energy of the two species. Unique phase behavior as compared to diblock polymer systems is displayed by the nanoparticle-polymer hybrid as will be discussed in more detail below.
Amphiphilic polymers in which two incompatible species are chemically joined have been used to investigate self-assembling mechanisms. Due to chemical connections these molecules do not macrophase separate, but rather microphase separate into complex morphologies. The equilibrium morphology of a self-assembled system is a result of a delicate balance between the free energy cost of the interfacial tension between the species and the conformational entropy loss of the molecules. The self-assembly of AB diblock copolymers, in particular, has been theoretically investigated in a number of studies due to the small parameter space that describes such systems.

In general, the system can be described by the degree of polymerization, the fraction of A monomers in the diblock and the incompatibility between the blocks. The phase diagram of melts of AB diblock copolymers has been theoretically constructed as a function of the block incompatibility and the fraction of A-monomers by strong segregation theory (SST) in the low temperature limit and self-consistent field theory (SCFT) for the weak to intermediate segregation regimes. We have extended our previous model that integrates a SCFT and a density functional theory (DFT) to investigate the phase behavior of amphiphilic hybrids that are formed by joining a linear flexible chain to spherical hard particles. The SCFT describes the thermodynamics of the chain portion, while the DFT describes the particle ordering. Using this method, we obtain the equilibrium morphologies and show that the phase behavior of these molecules differs significantly from that of diblock copolymers. Below, we will briefly describe the model and compare the unique phase behavior with self-assembly of diblock copolymers and micellization of surfactants.

**MATHEMATICAL MODEL**

Let us first define the system by a volume $V$ filled with $n$ “tadpole-like” molecules in which an A-like linear flexible chain is attached to a B-like spherical hard particle of radius $R$. The volume fraction of the A-like chain is
denoted f, and the total volume of each molecule is \( v_t = v_A + v_R = N/\rho_0 \) such that the volume of the linear chain part \( v_A = fN/\rho_0 \) and the volume of the sphere part \( v_R = (1 - f)N/\rho_0 = 4/3\pi R^3 \), where \( \rho_0^{-1} \) is the chain segment volume. For a given volume, f and R are not independent, and we specify R and determine f according to relation \( f = 1 - v_R/v_t \).

Now we define operators, which describe the distribution of each species:

\[
\hat{\Psi}_A(r) = \frac{N}{\rho_0} \sum_{\alpha} \int_0^T ds \delta(r - r_\alpha(s)), \tag{1}
\]

\[
\hat{\Psi}_B(r) = \frac{(1-f)}{v_R} \int_{|r'|<R} dr' \hat{\rho}_B(r' + r), \tag{2}
\]

\[
\hat{\rho}_B(r) = \frac{N}{\rho_0} \sum_{\alpha=1}^n \delta(r - r_\alpha(f) - R\hat{n}_\alpha), \tag{3}
\]

where subscripts A and B denote A-like coil and B-like sphere, and \( \rho_B \) is the distribution operator for the centers of the spheres. A unit vector \( \hat{n}_\alpha \) is also introduced in (3) to indicate the direction between the end of the coil, which is attached to the surface of the sphere, and the center of the sphere of the \( \alpha \)th tadpole. The unit vector for that tadpole is

\[
\hat{n}_\alpha = \sin \theta_\alpha \cos \phi_\alpha \hat{i} + \sin \theta_\alpha \sin \phi_\alpha \hat{j} + \cos \theta_\alpha \hat{k} \tag{4}
\]

where \( \hat{i} \), \( \hat{j} \), and \( \hat{k} \) are the three cartesian unit vectors. The angles \( \theta_\alpha \) and \( \phi_\alpha \) are measured from the z and x axes in the usual way for spherical coordinates.

After appropriate transformations, the partition function of the system can be written as

\[
Z = \int \mathcal{D}\Phi_A \mathcal{D}\Theta_B \mathcal{D}W_A \mathcal{D}W_B \mathcal{D}\Xi Q^\alpha \times \exp\left\{-\frac{\rho_0}{N} \int dr \left[ \chi N \Phi_B - W_A \Phi_A - W_B \Theta_B - \Xi (1 - \Phi_A - \Phi_B) \right] \right\}, \tag{5}
\]

where the partition function for a single tadpole Q is given by
\[ Q \equiv \int d\mathbf{h}_\alpha \int D\mathbf{r}_\alpha P[\mathbf{r}_\alpha; 0, f] \exp \left\{ -\int_0^f ds W_A(\mathbf{r}_\alpha(s)) - W_B(\mathbf{r}_\alpha(f) + R\mathbf{h}_\alpha) \right\}. \]  

(6)

We assume gaussian chains so the weight for individual configurations is given by

\[ P[\mathbf{r}_\alpha; s_1, s_2] = \exp \left\{ -\frac{3}{2N a^2} \int_{s_1}^{s_2} ds \left| \frac{d}{ds} \mathbf{r}_\alpha(s) \right|^2 \right\}. \]  

(7)

\( \alpha \) is the statistical segment length. By taking a mean field approximation of (5), we can get a free energy expression to which we add a correction to account for the steric interactions of the hard sphere parts of the tadpoles giving a free energy of

\[
\frac{NF}{\rho_0 k_B T V} = -\ln \left( \frac{QfN}{V \rho_0} \right) \\
+ \frac{1}{V} \int d\mathbf{r} [\chi N \varphi_A \varphi_B - w_A \varphi_A - w_B \rho_B] \\
- \xi (1 - \varphi_A - \varphi_B) + \rho_B \Psi (\varphi_B) 
\]  

(8)

where \( \Psi \) is the Carnahan-Starling free energy per particle, \( \varphi_B(\mathbf{r}) \) is a "smoothed" sphere density, \( k_B \) is Boltzmann’s constant, and \( T \) is the temperature. We can vary the free energy with respect to each of the independent functions to acquire the mean field equations, which allow us to solve the system self-consistently. As a result, we obtain the densities and fields for various possible morphologies, with the lowest free energy phase being the equilibrium state.

This model can be easily extended to describe an ABC copolymer in which an AB diblock copolymer is attached to a C type sphere. As before, we specify the radius \( R \) and determine the fraction of the diblock portion \( f \). An additional parameter \( f_A \), the fraction of the A block within the diblock, is needed to complete the description of the system. The total volume of the molecule is then \( V_T = V_A + V_B + V_R \), where \( V_A = f_A f N/\rho_0 \), \( V_B = (1-f_A) f N/\rho_0 \) and \( V_R = 4/3 \pi R^3 = (1-f)N/\rho_0 \). The distribution operators of each species are defined similar to 1-3 and the free energy is written as
\[
\frac{N F}{\rho_0 k_B T V} = -\ln \left( \frac{Q f N}{V \rho_0} \right) + \frac{1}{V} \int d\mathbf{r} \left[ \chi_{AB} \nabla \phi_A \nabla \phi_B + \chi_{AC} \nabla \phi_A \nabla \phi_C + \chi_{BC} \nabla \phi_B \nabla \phi_C \right] \\
- w_A \phi_A - w_B \phi_B - w_C \phi_C - \xi (1 - \phi_A - \phi_B - \phi_C) + \rho_0 \mathcal{V} \langle \phi_C \rangle,
\]

(9)

where additional terms are introduced to reflect additional interactions among different species.

We first consider the morphology of an AB tadpole system. Figure 1 shows the density contour plots of the coil and sphere portions in 2- and 3-dimensions. The volume of each tadpole in these figures is set equal to the volume of a linear chain, whose invariant polymerization index

\[N = N \rho_0^2 a^6 = 1000\]

where \(a\) is the statistical segment length. The sphere radius is set to \(R = 0.15 R_0\). Here, \(R_0\) is the root mean square end-to-end distance of the \(N = 1000\) chain. The incompatibility parameter is set to \(N_x = 30\), well above the order disorder transition value of \(\approx 10\).

This system corresponds to approximately 55 volume % coil and 45 volume % sphere for which AB composition a lamellar morphology is expected in a pure diblock system. However, a hexagonal close packed morphology is observed as can be clearly seen in Figure 1. The unusual departure in phase behavior from the diblock melt behavior can be attributed to the steric interaction between the spheres. For comparison with the diblock system, 1-D density profiles of the tadpole system and a diblock system of the same AB composition are shown in Figure 2. An obvious difference is the much shorter period of the AB domains of the tadpole system, indicating a less effective aggregation of the like-species. With the absence of B-like chains that can fill a void space among closely packed spheres, the system cannot aggregate and assemble into a lamellar morphology but must take on a hexagonal morphology. A close look at the sphere distribution in Figure 1 confirms that each circular regions rich in spheres indeed corresponds to a single sphere of radius \(R = 0.15 R_0\). This behavior also contrasts with micellization of surfactant molecules with a bulky head group. Rather than the head-to-tail ratio determining the micellar structure, steric interactions among spheres dominate, resulting in a possible formation of “unimolecular micelles.”
In order to circumvent the steric repulsion among spheres, we attach a diblock chain to a sphere such that the end of the diblock that is attached to the sphere is of the same species as the sphere. Figure 3 contains density profiles of a melt containing such molecules, with \( N_{x_{AB}} = 30 \), \( R = 0.1R_0 \) and \( f_A = 0.6 \). The parameters are selected so that the AB composition corresponds to one resulting in a lamellar morphology. Here, the A-like coil portion is approximately 48% of the total volume, while the B-like coil and the sphere portions make up the rest. Unlike the AB tadpole case, each species of these ABB tadpoles can aggregate to form a lamellar structure, as shown in Figure 3. In this case, steric repulsions, which prevent aggregation of spheres are shielded by sphere-like coils that can fill in the space between the spheres. The phase behavior of copolymers formed by attaching a flexible chain to a bulky head group differs significantly from that of diblocks due to steric interactions. These findings can be exploited to create materials requiring specific properties and geometries. For example, a solid particle with a specific index of refraction can be attached to an incompatible linear chain to create a regular array of particles for desired optical properties.

EXAMPLES

The most simple and direct route to prepare nanoparticle-polymer hybrids with structures similar to those shown in Figure 4 is a four step process:

1. Prepare a dispersion of nanoparticles in an appropriate solvent. For example 20 nm silica in water. A commercially available example is Nalco 1034A.

2. Silylate the particles with a very low surface coverage using a silane with a convenient additional reactive group, for example 3-10 vinyl trimethoxy silyl groups per particle.

3. Silylate the balance of the surface area of the particles using a silane that will render the surface phobic to the polymer block of choice. For example, trifluoropropyl trimethoxy silane renders the surface phobic to polydimethylsiloxane.
4. Couple the polymer chain of choice to the reactive silyl groups. For example, we coupled an SiH terminated polydimethylsiloxane polymer. The total molecular weight of all the polymer chains is chosen to obtain a volume fraction compared with the particle that will yield the desired microsegregated morphology. For 20 nm silica, we used polydimethylsiloxane chains with a total molecular weight of approximately 80,000 Daltons to give a volume ratio of about 5:1 particle-to-polymer and an expected cubic microstructure.

Using these steps we successfully prepared an amphiphilic nanoparticle-polymer hybrid material.

Alternatively, the fourth step can consist of growing polymer from the surface using, for example surface initiated polymerization. This process is inefficient in that the statistics of particle silylation yield a distribution of particles with varying numbers of silyl groups on them. Many particles are present that have zero silyl groups or a large number of silyl groups. Both of these detract from the desired self-assembly property by diluting and diffusing the microstructure. A more efficient process uses techniques disclosed in the literature to make particles with a different chemical functionality on each side of the particle as is depicted in the left side of Figure 4.

There are many approaches to do this. For example, the following publications:


disclose techniques for making particles with different chemical functionality on different portions of the particle, each of which is hereby incorporated by reference.

In one aspect, We have used a variation of the procedure disclosed in L. Nagle, D. Ryan, S. Cobbe, and D. Fitzmaurice, *Templated nanoparticle assembly on the surface of a patterned nanosphere*. Nano Letters, 2003. 3: p. 51-53, which is hereby incorporated by reference, to prepare 20 nm silica with reactive silyl groups attached selectively to one side. This process replaces steps 1 and 2 above. Steps 3 and 4 are carried out as above and as before, the polymer in step 4 can either be grafted to the reactive silyl groups or grown from initiator on the surface. We have carried out this process to prepare an improved amphiphilic nanoparticle-polymer hybrid material.
CLAIMS:

1. A nanoparticle-polymer hybrid comprising:
   a nanoparticle including a surface having a polymer grafted portion and
   a polymer incompatible portion;
   at least one polymer chain grafted to the surface of the nanoparticle;
   the at least one polymer chain and polymer incompatible portion of the
   nanoparticle interacting wherein the nanoparticle-polymer hybrid self-
   assembles into an ordered material.

2. The nanoparticle-polymer hybrid of Claim 1 wherein the
   nanoparticle includes a coating on the surface corresponding to the polymer
   incompatible portion.

3. The nanoparticle-polymer hybrid of Claim 2 wherein the
   coating comprises a uniform coating that selectively reacts with the at least one
   polymer chain at the polymer grafted portion of the nanoparticle.

4. The nanoparticle-polymer hybrid of Claim 2 wherein the
   coating comprises two different chemical species each selectively applied to
   the polymer grafted portion and polymer incompatible portion of the
   nanoparticle.

5. The nanoparticle-polymer hybrid of Claim 2 wherein the
   coating comprises a material selected from the group consisting of: alkyl thiols,
   silanes, hydrocarbons and small chain silicones.

6. The nanoparticle-polymer hybrid of Claim 1 wherein the
   nanoparticle comprises a material selected from the group consisting of: metal
   oxide particles, semiconductor particles and metal particles.
7. The nanoparticle-polymer hybrid of Claim 1 wherein the nanoparticle has a size of from 3 nanometers to 100 nanometers.

8. The nanoparticle-polymer hybrid of Claim 1 wherein the at least one polymer chain is covalently bonded to the nanoparticle.

9. The nanoparticle-polymer hybrid of Claim 1 wherein the at least one polymer chain comprises a plurality of polymer chains.

10. The nanoparticle-polymer hybrid of Claim 1 wherein the polymer chain comprises a material selected from the group consisting of: polystyrene, polybutadiene, polyisoprene, polycaprolactone, polyethyleneoxide, poly 2-vinyl pyridene, polydimethyl siloxane, biopolymers, including proteins, carbohydrates, and sugars.

11. The nanoparticle-polymer hybrid of Claim 1 wherein the volume fraction of the at least one polymer chain to the nanoparticle is from 25 to 75 percent.

12. The nanoparticle-polymer hybrid of Claim 1 further including a polymer miscible with the polymer chain for modifying a microstructure of the nanoparticle-polymer hybrid.

13. The nanoparticle-polymer hybrid of Claim 1 further including a polymer compatible with the outer surface of the nanoparticle for modifying a microstructure of the nanoparticle-polymer hybrid.

14. The nanoparticle-polymer hybrid of Claim 1 further including a diblockpolymer compatible with the outer surface of the nanoparticle for modifying a microstructure of the nanoparticle-polymer hybrid.
15. The nanoparticle-polymer hybrid of Claim 1 wherein the nanoparticle and polymer chain have a refractive index ratio of at least 1.1 for a continuous set of wavelengths of from 50 nanometers to 50 microns.

16. A nanoparticle-polymer hybrid comprising:
   a nanoparticle including an outer surface having a polymer grafted portion and a polymer incompatible portion;
   at least one polymer chain grafted to the outer surface of the nanoparticle at the polymer grafted portion;
   the at least one polymer chain and polymer incompatible portion of the nanoparticle interacting to define a microstructure of the nanoparticle-polymer hybrid that is independent in relation to other bulk properties of the nanoparticle.

17. A photonic bandgap material comprising:
   a nanoparticle-polymer hybrid comprising:
   a nanoparticle including an outer surface having a polymer grafted portion and a polymer incompatible portion;
   at least one polymer chain grafted to the outer surface of the nanoparticle at the polymer grafted portion;
   the at least one polymer chain and polymer incompatible portion of the nanoparticle interacting wherein the nanoparticle-polymer hybrid self-assembles into an ordered material and wherein the nanoparticle and polymer chain have a refractive index ratio of at least 1.1 for a continuous set of wavelengths of from 50 nanometers to 50 microns.

18. A blend of a nanoparticle-polymer hybrid and a block copolymer comprising:
   a nanoparticle including a surface having a polymer grafted portion and a polymer incompatible portion;
   at least one polymer chain grafted to the surface of the nanoparticle;
6 a block copolymer; and
7 wherein the blend self-assembles into an ordered material.
Figure 1
Figure 2