

NIRT – Nanoscale Engineering and Manufacture Effected Through Molecular Architecture and Structure

NSF NIRT Grant 0506309

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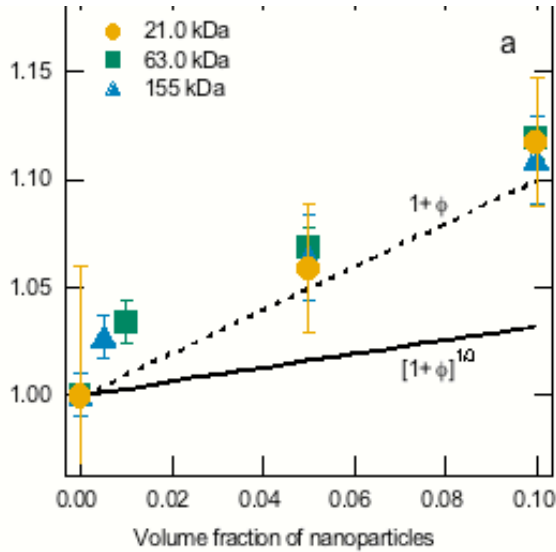
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Introduction. One of the necessary prerequisites for the successful application of nanotechnology is the ability to direct the self-assembly of nanoscale structures into ordered arrays. Presently, mere dispersion of nanoscale objects in polymeric materials is a critical manufacturing and technical hurdle, which must be overcome in a wide variety of industries. In this NIRT, we will develop technology that allows for dispersion, building on preliminary results that suggest interesting thermodynamics at the nanoscale, and for accurate control over the location of the dispersed nanoparticles leading to the next generation of nanostructured materials and devices. We will develop a range of strategies that allow for precise placement, and not merely dispersion, of nanoparticles within polymeric materials and devices that will enable this blossoming field to progress to the next level. The ultimate result of this research will be guided dispersion of nano-scale objects within the bulk, near surfaces or within confined geometries enabling the controlled design of materials and subsequent device manufacture.

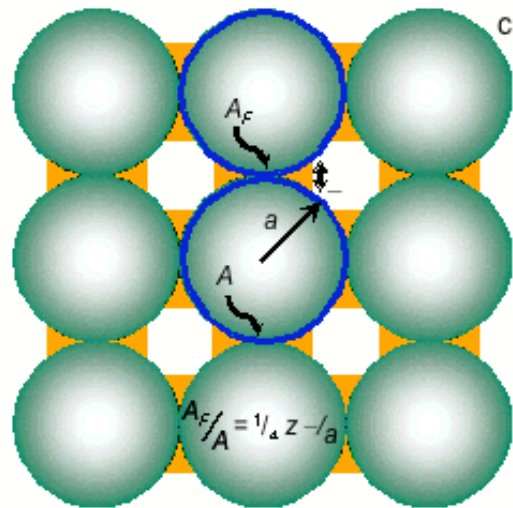
A unique team with expertise in synthetic chemistry (**Hawker, Wooley**), polymer science/characterization (**Assink, Celina**), computer simulation of nanomaterials (**Frischknecht, Tomanek**) and engineering (**Mackay**) has been assembled to develop an efficient and general approach to the dispersion and assembly of nanoscale objects such as: nanoparticles, decorated dendrimers, hyperbranched polymers, intramolecularly crosslinked polymers, uniquely shaped nano-objects (toroids) and fullerenes; within chemically dissimilar polymeric materials. The results of this research will allow new materials to be developed with improved properties and, ultimately, will serve as a general guide to the fabrication of devices based on nanoscale objects. Through application of principles determined from our fundamental studies, current technical challenges with nanoparticle-polymer dispersions will be overcome, permitting true realization of complex nanomaterials and nanodevices.

Dispersion. Traditionally, the dispersion of particles in polymeric materials has proven difficult and frequently results in phase separation and agglomeration. We have found that thermodynamically stable dispersion of nanoparticles into a polymeric liquid is enhanced for systems where the radius of gyration of the linear polymer is greater than the radius of the nanoparticle. Dispersed nanoparticles swell the linear polymer chains, resulting in a polymer radius of gyration which grows with the nanoparticle volume fraction. It is proposed that this entropically unfavorable process is offset by an enthalpy gain due to an increase in molecular contacts at dispersed nanoparticle surfaces, as compared to the surfaces of phase-separated nanoparticles. Even when the dispersed state is thermodynamically stable, it may be inaccessible

unless the correct processing strategy is adopted, which is particularly important for the case of fullerene dispersion into linear polymers. The results of this study are summarized in the figure below.¹



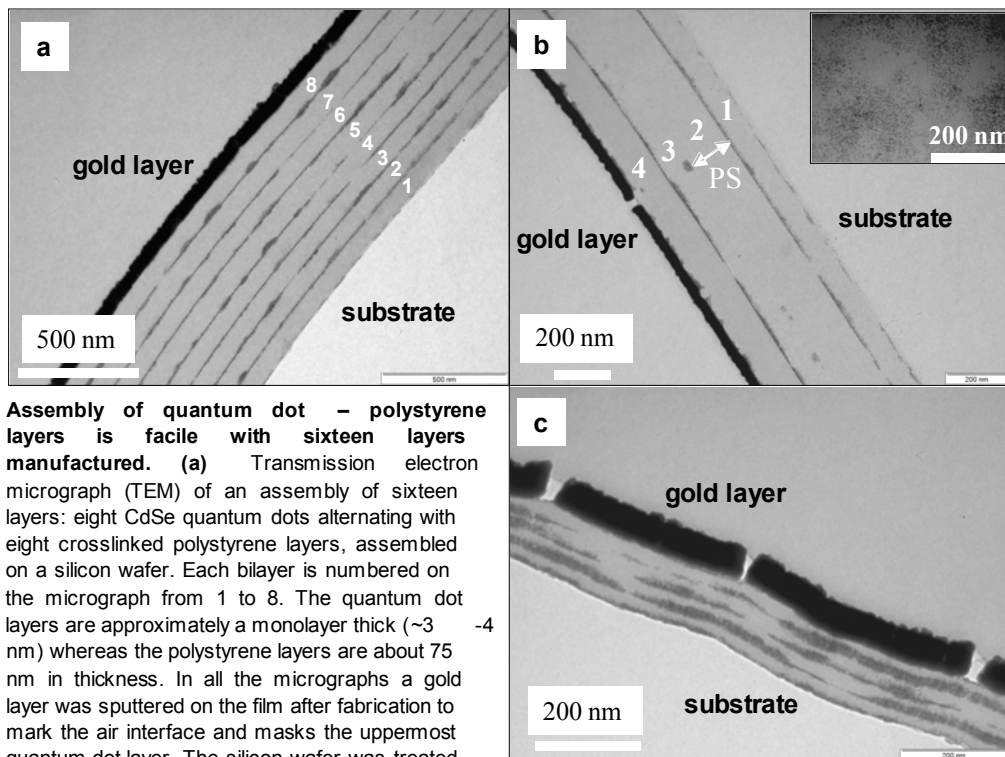
Nanoparticles swell the linear polymer yet the system remains stable. (a) The polymer radius of gyration (R_g), relative to that without nanoparticles (R_{g0}), for three different molecular mass linear polystyrenes: 21, 63, 155 kDa, as a function of 52.0 kDa tightly crosslinked polystyrene nanoparticle volume fraction (ϕ) demonstrating that nanoparticles do distort the polymer chain. The solid line represents the radius of gyration variation if the polymer density does not change upon mixing with nanoparticles and excluded volume strictly operates to distort the chain, $[1+\phi]^{1.02}$. Comparison of the data to an empiricism, $1+\phi$ shows reasonable agreement. (b) A polymer radius of gyration – nanoparticle radius phase diagram with the filled circles representing data where phase separation was detected and the open circles where miscibility occurs, open circles with a dash represent conditions where some agglomeration was detected by SANS, yet, large scale phase separation was not present. Squares are the C₆₀ fullerene – polystyrene system; circles, tightly crosslinked polystyrene nanoparticle polystyrene system; and triangles, dendritic polyethylene polystyrene system. The solid line represents the radius of gyration for the polymer directly related to the nanoparticle radius and the vertical dashed line the reptation tube radius. The phase stability does not seem to depend on the entanglement this length scale are miscible. The concentration used to generate between pure nanoparticles are expected to function only over a limited range (ϕ) over which dispersion forces operate even when the mean coordination number (z) is taken into account. Dissolution in a linear polymer will increase interactions over the entropically unfavorable linear polymer distortion.



structure or tube size since nanoparticles larger than a are not miscible. The concentration used to generate each data point was 2 – 10 wt%. (c) The forces (A_c) of the available surface area (A) due to the mean coordination number (z) is taken into account. Dissolution in a linear polymer will increase interactions over the total nanoparticle area to produce stable blends despite the entropically unfavorable linear polymer distortion.

Assembly. Self assembled, ultrathin films function as membranes and sensors as well as photovoltaic devices and structural elements, exemplifying their ubiquitous nature and application. Layered self-assembly of amphiphilic materials using the Langmuir-Blodgett procedure is well known and more recently electrostatically driven Layer-by-Layer or LbL assembly of polymeric multicomposites has been demonstrated. In the LbL approach the fabrication of polymeric multilayers is achieved by consecutive adsorption of polyanions and polycations and hence is driven by electrostatic forces to achieve monolayers whose thickness is dictated by the polymer geometry. Extension of the LbL method to self-assembly of alternating

layers of polymers and nanoparticles significantly extends the scope of this approach. However, the LbL approach cannot be used for non-polar or uncharged nanoparticles and polymers, which excludes a wide range of functional materials. We have found that self-assembly of nonpolar linear polymers and nanoparticles into layers with controllable, thickness can be fully realized using relatively simple and robust processing steps. Moreover, by controlling entropic and enthalpic driving forces we demonstrate controlled self-assembly of nanocomponent multilayers, promoting facile manufacture of a wide range of biomimetic and other fascinating nanostructures from nonpolar materials. This work is summarized in the figure below and will be published soon.



Assembly of quantum dot – polystyrene layers is facile with sixteen layers manufactured.

(a) Transmission electron micrograph (TEM) of an assembly of sixteen layers: eight CdSe quantum dots alternating with eight crosslinked polystyrene layers, assembled on a silicon wafer. Each bilayer is numbered on the micrograph from 1 to 8. The quantum dot layers are approximately a monolayer thick (~3 nm) whereas the polystyrene layers are about 75 nm in thickness. In all the micrographs a gold layer was sputtered on the film after fabrication to mark the air interface and masks the uppermost quantum dot layer. The silicon wafer was treated

with hydrofluoric acid and removed prior to microtoming. There are some quantum dots next to the substrate as discussed in the text. (b) Assembly of six layers formed by aging four layers to form three layers of CdSe quantum dots and three layers of crosslinked polystyrene. This sample was made by aging a polystyrene – quantum dot layer then spincoating a pure polystyrene layer on top and crosslinking it then repeating the process. The quantum dot layers are about a monolayer thick. The inset shows a TEM micrograph of the first layer normal to the substrate surface demonstrating a reasonably uniform film. (c) Assembly of eight layers: four CdSe quantum dots and four crosslinked polystyrene layers, assembled on a silicon wafer. In this case, the quantum dot layers are approximately 13 nm thick while the polystyrene layers are 15 nm thick to demonstrate control over the thickness of each layer is dictated by the initial conditions developed through the spincoating operation.

These two aspects of the NIRT represent the “engineering” aspects. Significant progress is being made in the theoretical and chemical thrusts and will be discussed in future reports.

References

[1] Mackay, M. E., Tuteja, A., Duxbury, P. M., Hawker, C. J., Van Horn, B., Guan, Z. B., Chen, G. H. & Krishnan, R. S. General strategies for nanoparticle dispersion. Science 311, 1740-1743 (2006).