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Title of Award: "Nanoparticles Stabilize Thin Polymer Films: A Fundamental Study to Understand the Phenomenon"

Prof. Michael E. Mackay – Principal Investigator
Dr. Amalie Frischknecht – Sandia National Laboratories
Dr. Erin McGarry – Postdoctoral Associate
Ms. Erica Tzu-Chia Tseng – Graduate Student

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Progress report

Project organization

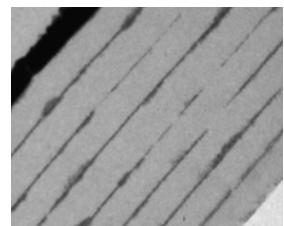
In this project we have successfully married an experimental – theoretical collaboration between the MSU research group and Sandia National Laboratories. To do this Prof. **Mackay** supervised a graduate student, Ms. Erica Tzu-Chia **Tseng**, who performed experiments, and a postdoctoral fellow, Dr. Erin **McGarrity**, who performed theoretical modeling in his laboratory and interacted with Dr. Amalie **Frischknecht**, a theoretician at SNL. Drs. **McGarrity** and **Frischknecht** had weekly teleconferences on Thursday mornings to discuss progress and had 2 - 3 face-to-face meetings per year. Dr. **Frischknecht** was funded on her part through **CINT** to allow this partnership. This unique collaborative effort of placing a theoretician within a group of experimentalists has tremendously aided experimental progress since the collaborators are intimately familiar with both the experimental and theoretical efforts. Furthermore development of new theoretical tools to interpret experimental results has resulted permitting rational verification and enhanced investigation of parameter space.

Beginning Fall 2008 the project was arranged differently. Prof. **Mackay** has taken a position in the Department of Materials Science at the University of Delaware (UD) where he is being considered for a named chair. The collaboration with Dr. **Frischknecht** continued as usual with Dr. **McGarrity** continuing his research at MSU. Ms. **Tseng** has moved to UD and continues here research without interruption. Dr. **McGarrity** has recently left the project to work on another project and a new postdoc has started on the project, Dr. Venkat **Padmanabhan**. Dr. **Padmanabhan** recently finished his PhD with Prof. **Kumar** at Columbia University and is uniquely capable to work on this project.

Summary of accomplishments

Accomplishment 1 - We have discovered that nanoparticles will self-assemble at solid substrates within a thin polymer film due to entropic forces exerted by the polymer molecule. The segregation forces are expected to be quite strong, we have estimated its energy to be of order $10 - 100 k_B T$ per nanoparticle, to create an effective coating that makes the polymer film stable on otherwise unwettable substrates.¹⁻³ The segregation occurs since a segment of the polymer molecule gains degrees of freedom by pushing the nanoparticles to the substrate, which only lose three degrees of translation entropy, and laying on the nano-rough carpet of nanoparticles. So, film stability results since the energy gain through dewetting is less than the energy cost in disassembling the nanoparticle layer. We have used density functional theory (DFT) calculations of hard spheres mixed with a hard sphere polymer to demonstrate that entropic segregation is entirely possible.³ Furthermore, theory shows that as more and more nanoparticles are forced to the substrate a surface concentration is reached where a first order entropic phase transition occurs and a particle monolayer results excluding the polymer molecules from the wall. This self assembly can be useful in a variety of fields such as advanced coatings, sensors,⁴ solar cells, etc.

Accomplishment 2 - We found the above phenomenon can be used in other applications and were able to extend it to make multi-layered assemblies⁵ similar in effect to layer-by-layer assembly.⁶ In contrast, our process allows variation of each layer's thickness, an important nanoscale design variable. The figure to the right demonstrates such an assembly where a layer of CdSe quantum dots and cross-linkable polystyrene were spin coated onto a substrate, the film was softened by an increase in temperature to allow self-assembly and crosslinking of the polymer which made it insoluble upon subsequent exposure to solvent. The process was repeated seven more times, as shown in the figure, to create a layered assembly where each bilayer was ~ 75 nm thick. The amount of either component in any given layer can be varied to generate a given thickness, as can be the overall thickness of each bilayer, to give precise control of the multilayered assembly unlike what can be accomplished in layer-by-layer assembly. We have denoted this process as SAMON: *Self-Assembled Multilayers Of Nanocomponents*, and can be used in optical devices, dielectric coatings, tandem solar cells, etc.



Accomplishment 1 – Inhibition of dewetting by nanoparticle segregation

Experimental results and discussion - Neutron reflectivity measurements have been used to show that polystyrene nanoparticles (see Figure 1a) are uniformly distributed in the polystyrene film before annealing, yet, after annealing they are found to separate to the solid substrate and to retard the dewetting kinetics of the linear polymer.² A crude estimate of the fractional aerial coverage (θ) of the nanoparticles at the substrate, based on a simple mass balance, is given by

$$\theta = (h/2a) \times \phi \quad (1)$$

where h is the film thickness, a , the nanoparticle radius and ϕ , the bulk nanoparticle volume fraction. $\theta \approx 1$ corresponds to a dense packed monolayer of nanoparticles at the substrate. It was shown in our previous work,² and is further demonstrated in our more recent study,¹ that dewetting is severely retarded for nanoparticle volume fractions corresponding to a segregated nanoparticle monolayer or more.

Neutron reflectivity (R) profiles for nanoparticle blend films containing 5-20 wt% nanoparticles and thickness approximately 45 nm were annealed in air for 24 hrs at a temperature of 160°C, except the 5% blend for which annealing was restricted to 2 hrs to limit dewetting. Fits to the neutron reflectivity data were based on a two layer model (as will be justified below), where the top layer is composed of pure (deuterated) linear polymer (dPS 63 kD) and the bottom layer consists of both the linear polymer and nanoparticles. For example, a 39 nm thick film of a 10 wt% nanoparticle blend was fitted to the model and one finds the scattering length density (SLD) of the layer next to the substrate to be $4.72 \times 10^{-6} \text{ \AA}^{-2}$ whereas the top layer has an SLD of $6.42 \times 10^{-6} \text{ \AA}^{-2}$. In fitting this reflectivity profile, the pure polymer-nanoparticle rich layer interface roughness was found to be 4 nm and the nanoparticle layer thickness was 6.2 nm. Of course, the roughness relative to the layer thickness is large and so may not have physical significance. The resolution of the Q-vector ($\Delta Q/Q$) for the instrument was also employed as a fitting parameter and was found to be approximately 0.03, a reasonable value. Here Q is given by, $Q = 4\pi \sin(\Theta/2)/\lambda$, Θ is the scattering angle and λ is the neutron wavelength.

A test of alternative models is presented in Figure 1b for the case of the 39 nm thick film containing 10 wt% nanoparticles, where a plot of RQ^4 versus Q for the data and various modeling results are presented. This type of plot is useful when considering sharp interfaces and R should decay as Q^4 when they are present. Three models are compared to the data in this figure, firstly a model where complete phase segregation to the substrate occurs as discussed above, secondly, a case of homogeneous distribution of nanoparticles in the film and thirdly, a case where the nanoparticles segregate to the air interface. Clearly, the latter model does not predict the observed reflectivity profile. The case of homogeneous distribution shows little difference to the observed reflectivity at low Q but does not represent the data at high Q . Only the case of nanoparticles separating to the hard substrate gives a satisfactory agreement to the observed reflectivity at both low and high values of the wave vector.

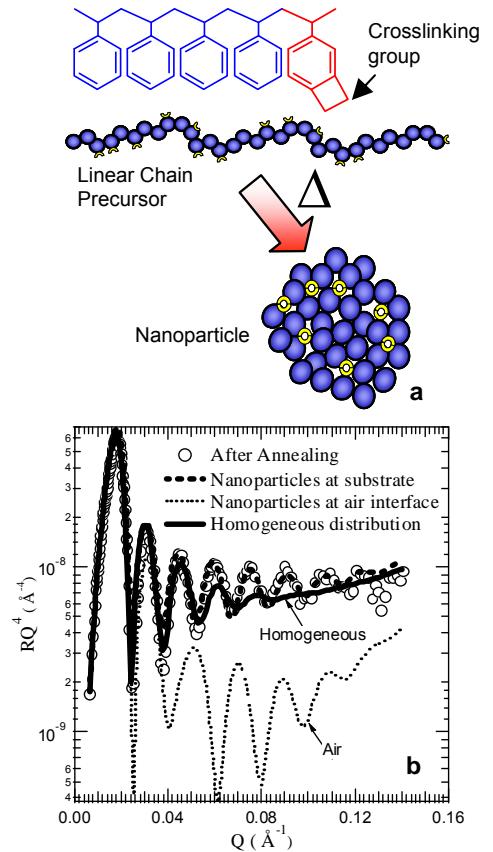


Figure 1. a. Synthesis of polystyrene nanoparticles occurs by crosslinking pendent butane groups of a linear precursor chain by dripping a dilute solution into hot solvent that activates the crosslinking process. b. Reflectivity multiplied by reflectance wave vector to the fourth power (RQ^4) versus Q using a 39 nm thick film, and a comparison of fits to three different models placing the nanoparticles at the substrate or air interface or homogeneously distributed throughout the film. Protonated polystyrene nanoparticles were mixed with deuterated linear polystyrene and the assembly process activated.

Theoretical rationalization: Simple model - In polystyrene nanoparticle/linear polystyrene systems, segregation of the nanoparticles to the substrate is driven by an entropy gain for the entire system,⁷ a mechanism similar to that arising when low molecular weight polymers are mixed with high molecular weight polymers of the same composition.⁸ A simple argument can be made⁷ to justify this segregation by noting that the monomer units in a linear polymer will gain $\alpha k_B T[\alpha/\sigma]^3$ of entropy when they move from the solid substrate and push a nanoparticle down. Here α is the number of degrees of freedom gained by a given monomer unit, k_B is the Boltzmann constant, T is temperature and σ is the size of a monomer unit (the quantity $[\alpha/\sigma]^3$ represents the number of monomer units that gain entropy). The nanoparticle itself will lose $\sim k_B T$ worth of translational entropy while segregation from the blend costs $\varepsilon [\alpha/\sigma]^2$ of mixing free energy⁹ to account for monomer interactions with the nanoparticle surface, ε is of order $0.1 - 1 k_B T$ for dispersion forces. A simple balance between these thermodynamic components shows that $\alpha[\alpha/\sigma]^3 > 1 + [\varepsilon/k_B T][\alpha/\sigma]^2$ for segregation, requiring that a monomer unit in a linear chain near the substrate must gain $0.01 - 0.1$ degrees of freedom due to constraint release when nanoparticle segregation occurs. It is expected, however, that α is of order one demonstrating that an entropy based mechanism is certainly capable of driving segregation to an interface with energy $10 - 100 k_B T (\sim \alpha k_B T[\alpha/\sigma]^3)$, as is consistent with nanoparticle segregation observed in self-consistent field calculations of nanoparticle segregation in blends¹⁰ and also with density functional calculations we are presently performing in our group as described below. **Once the nanoparticles segregate to the interface, we find that any surface can be wetted, even very low energy surfaces since the assembly energy is so large and the nanoparticle layer acts as an effective coating.**

Theoretical rationalization: More comprehensive DFT model - We employed a computationally efficient, classical density functional theory (DFT) to explore the phase behavior of the model system of polystyrene nanoparticles distributed in linear polystyrene.³ DFTs can capture the microscopic structure and thermodynamic behaviors of complex fluids^{11, 12} and are based on minimization of a grand potential free energy functional. Since the minimization results in the grand potential free energy of the system, DFTs are well-suited to the study of phase behavior. Although this is an efficient DFT we have used **43,220.87 h of CPU time** in calculations at Sandia National Laboratories, a little under 5 years on a single processor.

We use a density functional that is based on the fundamental measure theory of hard sphere liquids, pioneered by Rosenfeld,¹³ where both the nanoparticles and the polymer segments are treated as hard spheres. Bonding constraints between the polymer segments are enforced using the Wertheim-Tripathi-Chapman (WTC) bonding functional,^{14, 15} which is based on Wertheim's thermodynamic perturbation theory (TPT1).^{16, 17} The DFT is formulated in an open (μ VT) ensemble with the grand potential for the hard sphere/polymer blend given by

$$\Omega[\rho_\alpha(r)] = F_{id}[\rho_\alpha(r)] + F_{hs}[\rho_\alpha(r)] + F_{ch}[\rho_\alpha(r)] + \sum_\alpha \int dr \rho_\alpha(r) [V_\alpha(r) - \mu_\alpha] \quad (2)$$

where the terms on the right-hand side represent the Helmholtz free energies for the ideal gas, the hard sphere, and the chain constraints. The final term is the Legendre transformation where the μ_α are the site chemical potentials and $V_\alpha(r)$ is an external field. The exact form of the Rosenfeld hard sphere term, F_{hs} , can be found in Rosenfeld *et al.*¹⁸ with a more accessible derivation of this functional given in Roth *et al.*¹⁹ We implemented a form of the chain free energy functional F_{ch} (Equation 22 from Tripathi and Chapman¹⁵) to keep track of, and solve explicitly for, segment densities by treating each segment as a separate species.

The surface free energy of a blend with $N = 40$ is shown in Figure 2a, where the surface free energy is defined as $\Omega_s[\rho_\alpha(r)] = \Omega[\rho_\alpha(r)] - \Omega_{bulk}$, and Ω_{bulk} is the free energy of a homogeneous bulk system with the same packing fraction and composition. The dark curve with "x" markers corresponds to the stable solutions of the free energy minimization for the mixture. There is a distinct change in slope in the curve at a density of $\rho_n^* \sigma_p^3 = 0.01263$, which indicates a first order phase transition. The light part of the curve represents the metastable and unstable branches of the phase space explored by the continuation solver. The point at which the curve crosses itself has two solutions with distinct morphologies. The dashed line represents the free energy of a neat polymer system with the same length ($N = 40$) and packing fraction. Note that the addition of nanoparticles reduces the free energy of the system.

The excess adsorption Γ_α is shown in Figure 2b, where Γ_α is defined as $\Gamma_\alpha = \int dz(\rho_\alpha(z) - \rho_\alpha)$. The vertical lines indicate the sudden jump in adsorption as the nanoparticle density is increased through the phase transition. This jump shows the polymer being expelled from the wall by the nanoparticles with the van der Waals loops being clear indicators of a first order transition.

The two coexisting density profiles found at the phase transition are shown in Figure 2c & d. A density profile converged at the coexistence density (ρ_n^*) from a profile at a slightly lower nanoparticle density is shown in Figure 2c. The density profile is typical for a dense liquid where both the nanoparticles and polymer have pronounced peaks near the substrate, yet, the polymer peak is closer to the substrate because of the smaller size of its segments. Converging to ρ_n^* from a higher particle density (see Figure 2d), we find that the polymer has been almost completely excluded from the vicinity of the substrate, and there is a large peak in the nanoparticle density adjacent to the substrate, indicating a large adsorption of nanoparticles which of course is evident in Figure 2b. The height of the first peak in the nanoparticle density does not change significantly as we add nanoparticles above the transition density, so the structure of the monolayer remains the same above the transition. The contact densities are in reasonable agreement with the pressure sum rule $p/kT = \sum_\alpha \rho_\alpha (z = \sigma_\alpha/2 + \sigma_p/2)$.

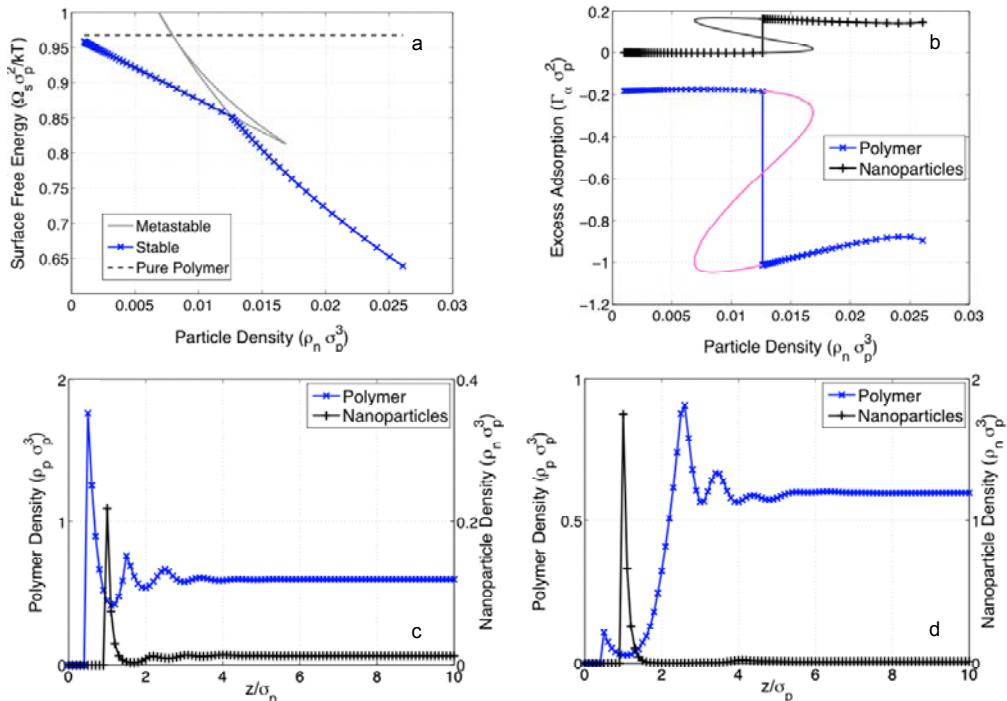


Figure 2. **a.** Surface free energy versus nanoparticle density for $N = 40$ and $\eta = 0.3665$. The dark curve with the “x’s” indicates stable configurations. The abrupt change in slope of this curve at $\rho_n^* \sigma_p^3 = 0.01263$ is indicative of a first order phase transition. Solutions in the metastable and unstable regions are shown by the light curve. The dashed line indicates the free energy of a neat polymer system with $N = 40$ and $\eta = 0.3665$. **b.** Excess adsorption of blend components as a function of nanoparticle density. The “x’s” and “+’s” indicate the polymer and nanoparticles, respectively. The light colored parts of the curves correspond to the meta/unstable branches. **c & d.** Density profiles for polymer (“x’s” -- left scale) and nanoparticles (“+’s” -- right scale), with $N = 40$ with $\eta = 0.3665$ at the phase transition ($\rho_n^* = 0.01263$). These profiles were computed by setting the density to ρ_n^* and restarting with an initial guess profile which was converged at a lower (**c**) and higher (**d**) density.

Thus we have found a first order phase transition in which the polymer is pushed away from the substrate and is replaced by the nanoparticles. Integrating under the first peak ($0 \leq z/\sigma_p \leq 2$) of the nanoparticle density profile in Figure 2d gives a density per unit area of $0.2866/\sigma_p^2$, which corresponds to a densely packed monolayer on the surface with an areal coverage of 0.9. To our knowledge this is the first report of the calculation of an **entropically-driven** surface phase transition in an **athermal** polymer/nanoparticle blend.

Accomplishment 2 – Self assembled multilayers of nanocomponents

We show that multilayers formed from CdSe quantum dots and linear polystyrene are controlled by the interplay between surface energy, dispersion forces and entropy. In this system, the nanoparticles primarily segregate to the air interface yet multilayer fabrication remains facile. Although not discussed below, we have found that multilayers can be fabricated merely by having different architecture components of the same chemical compound (*i.e.* sphere versus coil). In addition, multilayers of two incompatible polymers, namely linear polystyrene and linear polymethylmethacrylate (PMMA), where CdSe quantum dots are used to stabilize the multilayer, can also be assembled.⁵

Multilayer assembly – Phase segregation of the quantum dots from linear polystyrene, in thin films, is clearly evident in transmission electron microscopy (TEM) images shown in Figure 3. We note that these quantum dots are completely soluble in bulk polystyrene, as occurs for others systems where nanoparticle architecture enables bulk miscibility, with a particularly notable case being dendritic polyethylene²⁰ in polystyrene⁹ and magnetite in polystyrene.²¹

The quantum dots primarily assemble at the air interface in this system with the exception of the first layer, layer 1 in the figure, where they are at both interfaces. This is made clear by viewing Figure 3b which has the following layer deposition scheme: **layer 1**, polymer + quantum dots; **layer 2**, pure polymer; **layer 3**, polymer + quantum dots; **layer 4**, pure polymer; with each layer being processed by thermal aging after spincoating to activate the crosslinking process between polymer molecules, which stabilizes this layer, before the subsequent layer is deposited. Some quantum dots have assembled at the substrate interface in layer 1, yet, most have segregated to the air interface as discussed above.

The assembly is easily described by careful consideration of the Hamaker coefficient for trilayers making-up a multilayer assembly. If the constant is negative then that trilayer is stable with the effective interface potential positive to ensure stability.²² If we consider a trilayer of air (component 1) – quantum dots (3) – polystyrene (2) then one can determine the sign of the Hamaker constant (A_{132}) using,²³ $A_{132} \sim [n_1^2 - n_3^2] \times [n_2^2 - n_3^2]$, which is a good heuristic for nonconducting materials. Here n_i is the refractive index of component i with the following approximate values: 1.0 (air), 1.54 (quantum dots) and 1.59 (polystyrene). The value for the quantum dots' refractive index was arrived at by computing a volume average of a CdSe inner core with a 2.2 nm radius (refractive index of 2.8) surrounded by an oleic acid layer which is 2.5 nm thick (refractive index of 1.4). The oleic acid layer thickness was determined by dynamic light scattering of a dilute toluene solution and is a reasonable value based on the chemical structure. With these values, the ordering of air – quantum dots – polystyrene is stable while others are not. Here the dielectric or surface energy forces are stronger than the entropic forces mentioned above to push the assembly to the air interface.

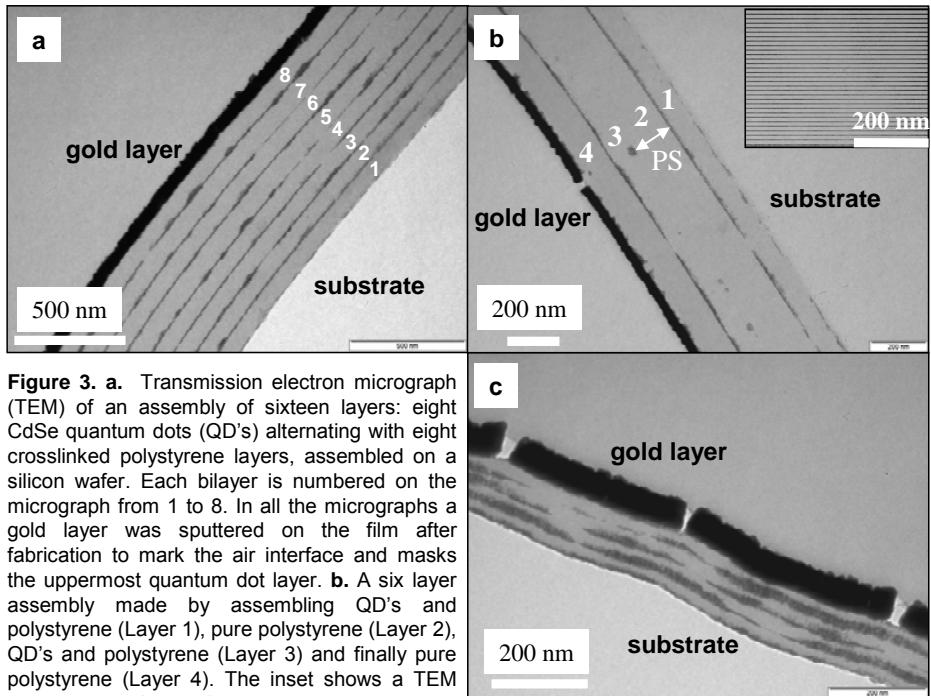


Figure 3. **a.** Transmission electron micrograph (TEM) of an assembly of sixteen layers: eight CdSe quantum dots (QD's) alternating with eight crosslinked polystyrene layers, assembled on a silicon wafer. Each bilayer is numbered on the micrograph from 1 to 8. In all the micrographs a gold layer was sputtered on the film after fabrication to mark the air interface and masks the uppermost quantum dot layer. **b.** A six layer assembly made by assembling QD's and polystyrene (Layer 1), pure polystyrene (Layer 2), QD's and polystyrene (Layer 3) and finally pure polystyrene (Layer 4). 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 QD's and four polystyrene where the quantum dot layers are thicker than previous assemblies and the polystyrene are thinner (both ~ 15 nm).

Much thicker quantum dot layers and thinner polymer layers can also be formed as demonstrated in Figure 3c where ca. 15 nm thick quantum dot layers have been assembled with ~15 nm thick crosslinked polystyrene. Again, the first layer shows a thin quantum dot layer at the substrate with most of them located at the upper part of this film. Subsequent films show alternating layers of the two components which are not as coherent as the layers formed with a lesser amount of quantum dots, Figures. 3 a&b as well as the inset of Figure 3b, although they are certainly distinct. We believe the layers can be further refined through optimization of the processing conditions. In summary, we are able to assemble nanoparticles in multilayers to either the air interface or the solid interface in a controllable manner.

Planned activities

The first main accomplishment, as a result of this funding, are that nanoparticles can be made to assemble at a solid substrate or the air interface dependent on their dielectric properties, as well as entropic forces. When this occurs the film can be made stable on many substrates even when dewetting is expected since the assembly energy of the layer is strong enough to resist the dewetting forces. The second accomplishment is that the assembly process can be repeated allowing layered structures to be manufactured as a more flexible alternative to layer-by-layer assembly.

The proposed activities will be conducted by the researchers to build on these discoveries to develop a more fundamental understanding of the process through development of new theoretical tools and to generalize the self assembly process from two-dimensions to one- and three-dimensions. Specifically we propose to:

1. Perform one-, two- and three-dimensional assembly of nanoparticles in thin polymer films
 - o We have recently done this and will continue on it. A high profile publication is being written. These results show that this will be a fruitful avenue of research.
2. Achieve directed assembly of nanoparticles between given objects
 - o Preliminary results show that we can assemble nanoparticles in one dimension along an object and we will work on assembling them between objects. This too looks like a fruitful project.
3. Develop theoretical capabilities describing nanoparticle filled polymer films between a solid substrate and vapor
 - o This will be Dr. Padmanabhan's first project, albeit a difficult one.
4. Use PRISM theory to calculate bulk nanoparticle – polymer interactions.
 - o We have recently written a new PRISM code that allows the polymer to adopt any configuration rather than that when no nanoparticles are present. The polymer molecules swell as seen in our experiments, we will continue this study in tandem with the thin film work since it allows us to more fully understand polymer – nanoparticle interactions.

Publications

Published manuscripts

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** (2006) 1740-1743.

Krishnan, R. S., Mackay, M. E., Duxbury, P. M., Pastor, A., Hawker, C. J., Van Horn, B., Asokan, S. & Wong, M. S. Self-assembled multilayers of nanocomponents. *Nano Letters* **7** (2007) 484-489.

Krishnan, R. S., Mackay, M. E., Duxbury, P. M., Hawker, C. J., Asokan, S., Wong, M. S., Goyette, R. & P. Thiagarajan. Improved polymer thin-film wetting behavior through nanoparticle segregation to interfaces. *J. Phys.: Cond Matter* **19** 356003 (2007).

McGarrity, E. S., Frischknecht, A. L., Frink, L. J. D. & Mackay, M. E. Surface-induced First Order Transition in Athermal Polymer/Nanoparticle Blends. *Phys Rev Letters* **99** (2007) 238302 -1-4.

A. Tuteja, P. M. Duxbury and M. E. Mackay, "Multifunctional nanocomposites with reduced viscosity," *Macromolecules*, **40** (2007) 9427-9434.

E. S. McGarrity, A. L. Frischknecht and M. E. Mackay, "Phase behavior of polymer/nanoparticle blends near a substrate," *J. Chem. Phys.*, **128** (2008) 154904-1 - 154904-10.

E. S. McGarrity, P. M. Duxbury, M. E. Mackay and A. L. Frischknecht, "Calculation of entropic terms governing nanoparticle self-assembly in polymer films," *Macromolecules*, **41** (2008) 5952-5954.

M. A. Yaklin, P. M. Duxbury and M. E. Mackay, "Control of nanoparticle dispersion in thin polymer films," *Soft Matter*, **4** (2008) 2441 - 2447.

J. W. Liu, M. E. Mackay and P. M. Duxbury, "Nanoparticle formation by crosslinking a molecule," *Europhys Letters*, **84** (2008) 46001.

Manuscripts that have been written and are under final revision and primarily funded by this grant

T.E. Bohnsack, E. S. McGarrity, M.E. Mackay, A.L. Frischknecht and P.M. Duxbury, "Thermal Conformational Changes of Single Polystyrene Molecules on a Substrate," for PRL (The simulations are extremely difficult for this and we are delaying publication until we are sure of the results.)

Manuscripts that have been written and are under final revision and partially funded by this grant

Melissa A. Holmes and Michael E. Mackay, "Dynamics and Stability of Solvent Annealed Polymer Films: Influence of Molecular Weight and Film Thickness," for *J. Chem. Phys.*

Tiffany E. Bohnsack, Erin S. McGarrity, Michael E. Mackay, "A Softening Effect Exhibited in Single Polystyrene Nanoparticles and Macromolecules on Solid Substrates," for PRL

Manuscripts that will be written soon and primarily funded by this grant

E. S. McGarrity, T. E. Bohnsack, J. Liu., P. M. Duxbury, and M. E. Mackay, "Single molecule dynamics of polystyrene adsorbed on a substrate." In preparation, 2007.

E. S. McGarrity, T. E. Bohnsack, T. C. Tseng, J. W. Kiel, P. M. Duxbury, M. E. Mackay, M. Pasqualli, and M. S. Wong, "Directed segregation and nanoparticle assembly in one, two and three dimensions." in preparation, 2009.

A.L. Frischknecht, E.S. MacGarrity and M.E. Mackay, "PRISM calculations that show polymer chain swelling in the presence of nanoparticles," in preparation 2009.

People working on this project

Graduate students – R.S. Krishnan (graduated with a PhD, May 2006)
Erica Tseng (started in 2006)

Postdoc – Dr. Erin S. McGarry (ended February 2009)
Dr. Venkat Padmanabhan (started March 3, 2009)

Collaborator – Dr. Amalie Friscknecht, Sandia National Laboratories & CINT

Current and pending support

<p>The following information should be provided for each investigator and other senior personnel. Failure to provide this information may delay consideration of this proposal.</p>			
<p>Investigator: Prof. Michael E. Mackay</p>		<p>Other agencies (including NSF) to which this proposal has been/will be submitted. None</p>	
<p>Support: <input checked="" type="checkbox"/> Current <input type="checkbox"/> Pending <input type="checkbox"/> Submission Planned in Near Future</p>		<p><input type="checkbox"/> *Transfer of Support</p>	
<p>Project/Proposal Title: NIRT- Nanoscale Engineering and Manufacture Effected Through Molecular Architecture and Structure (M.E. Mackay (PI), D. Tomanek (MSU), C. Hawker (UCSB), K. Wooley (Wash U- St. L)</p>			
<p>Source of Support: NSF-NIRT Total Award Amount: \$1,310,000 Total Award Period Covered: 2005-2009</p>			
<p>Location of Project: University of Delaware Person-Months Per Year Committed to the Project. Cal: Acad: Sumr: 1</p>			
<p>Support: <input checked="" type="checkbox"/> Current <input type="checkbox"/> Pending <input type="checkbox"/> Submission Planned in Near Future</p>		<p><input type="checkbox"/> *Transfer of Support</p>	
<p>Project/Proposal Title: Nanoparticles Stabilize Thin Polymer Films; A fundamental study to understand the phenomenon (Mackay)</p>			
<p>Source of Support: DOE-BES Total Award Amount: \$525,000 Total Award Period Covered: 2008-2011</p>			
<p>Location of Project: University of Delaware Person-Months Per Year Committed to the Project. Cal: Acad: Sumr: 1</p>			
<p>Support: <input checked="" type="checkbox"/> Current <input type="checkbox"/> Pending <input type="checkbox"/> Submission Planned in Near Future</p>		<p><input type="checkbox"/> *Transfer of Support</p>	
<p>Project/Proposal Title: World Materials Network- Healing Polymers: The self-assembly approach (with Stuart Rowan (CWRU)-PI)</p>			
<p>Source of Support: NSF Total Award Amount: \$566,836 Total Award Period Covered: 2006-2009</p>			
<p>Location of Project: Case Western Research University and University of Delaware Person-Months Per Year Committed to the Project. Cal: Acad: Sumr: 0.5</p>			
<p>Support: <input checked="" type="checkbox"/> Current <input type="checkbox"/> Pending <input type="checkbox"/> Submission Planned in Near Future</p>		<p><input type="checkbox"/> *Transfer of Support</p>	
<p>Project/Proposal Title: Center for Integrated Nanotechnology (CINT)- Effects of nanoparticles on polymer film wetting (with Dr. Frischknecht)</p>			
<p>Source of Support: Sandia National Laboratories/Los Alamos Laboratory Total Award Amount: \$0 Total Award Period Covered: 2008-2009</p>			
<p>Location of Project: University of Delaware Person-Months Per Year Committed to the Project. Cal: Acad: Sumr:</p>			
<p>Support: <input checked="" type="checkbox"/> Current <input type="checkbox"/> Pending <input type="checkbox"/> Submission Planned in Near Future</p>		<p><input type="checkbox"/> *Transfer of Support</p>	
<p>Project/Proposal Title: Modification of Polymer Rheology and Physical Properties by Nanoparticle Incorporation (Mackay)</p>			
<p>Source of Support: BASF Total Award Amount: \$320,000 Total Award Period Covered: 2006-2010</p>			
<p>Location of Project: University of Delaware Person-Months Per Year Committed to the Project. Cal: Acad: Sumr: 1</p>			
<p>*If this project has previously been funded by another agency, please list and furnish information for immediately preceding funding period.</p>			

<p>The following information should be provided for each investigator and other senior personnel. Failure to provide this information may delay consideration of this proposal.</p>			
<p>Investigator: Prof. Michael E. Mackay</p>		<p>Other agencies (including NSF) to which this proposal has been/will be submitted: None</p>	
<p>Support: <input type="checkbox"/> Current <input checked="" type="checkbox"/> Pending <input type="checkbox"/> Submission Planned in Near Future</p>		<p><input type="checkbox"/> *Transfer of Support</p>	
<p>Project/Proposal Title: Indirect Reinforcement of Nanocomposites</p>			
<p>Source of Support: ARO</p>			
<p>Total Award Amount: \$313,669</p>		<p>Total Award Period Covered: 2009-2012</p>	
<p>Location of Project: University of Delaware</p>			
<p>Person-Months Per Year Committed to the Project.</p>		<p>Cal:</p>	<p>Acad:</p>
		<p>Sumr: 1</p>	
<p>Support: <input type="checkbox"/> Current <input checked="" type="checkbox"/> Pending <input type="checkbox"/> Submission Planned in Near Future</p>		<p><input type="checkbox"/> *Transfer of Support</p>	
<p>Project/Proposal Title: Nanoparticles violate the Stokes-Einstein relation</p>			
<p>Source of Support: NSF</p>			
<p>Total Award Amount: \$373,659</p>		<p>Total Award Period Covered: 2009 - 2012</p>	
<p>Location of Project: University of Delaware and Lincoln University</p>			
<p>Person-Months Per Year Committed to the Project.</p>		<p>Cal:</p>	<p>Acad:</p>
		<p>Sumr: 1</p>	
<p>Support: <input type="checkbox"/> Current <input checked="" type="checkbox"/> Pending <input type="checkbox"/> Submission Planned in Near Future</p>		<p><input type="checkbox"/> *Transfer of Support</p>	
<p>Project/Proposal Title: Advanced Solar energy Conversion Through Control of Interfaces and Surfaces: An Energy Frontier Research Center (Opila (PI) + 24 others)</p>			
<p>Source of Support: DOE</p>			
<p>Total Award Amount: \$21,871,900</p>		<p>Total Award Period Covered: 2009 - 2014</p>	
<p>Location of Project: University of Delaware</p>			
<p>Person-Months Per Year Committed to the Project.</p>		<p>Cal:</p>	<p>Acad:</p>
		<p>Sumr: 1</p>	
<p>Support: <input type="checkbox"/> Current <input type="checkbox"/> Pending <input type="checkbox"/> Submission Planned in Near Future</p>		<p><input type="checkbox"/> *Transfer of Support</p>	
<p>Project/Proposal Title:</p>			
<p>Source of Support:</p>			
<p>Total Award Amount:</p>		<p>Total Award Period Covered:</p>	
<p>Location of Project:</p>			
<p>Person-Months Per Year Committed to the Project.</p>		<p>Cal:</p>	<p>Acad:</p>
		<p>Sumr:</p>	
<p>Support: <input type="checkbox"/> Current <input type="checkbox"/> Pending <input type="checkbox"/> Submission Planned in Near Future</p>		<p><input type="checkbox"/> *Transfer of Support</p>	
<p>Project/Proposal Title:</p>			
<p>Source of Support:</p>			
<p>Total Award Amount: \$</p>		<p>Total Award Period Covered:</p>	
<p>Location of Project:</p>			
<p>Person-Months Per Year Committed to the Project.</p>		<p>Cal:</p>	<p>Acad:</p>
		<p>Sumr:</p>	
<p>*If this project has previously been funded by another agency, please list and furnish information for immediately preceding funding period.</p>			

Cost status

The funding for this grant is for three years at a\$150,000 per year and started 4/1/2005. Presently we are on budget renewed the grant. The approved budget for the renewed grant is on the following page.

DOE F 4620.1 (04-93) All Other Editions Are Obsolete	U.S. Department of Energy Budget Page (See reverse for Instructions)			OMB Control No. 1910-1400 OMB Burden Disclosure Statement on Reverse	
ORGANIZATION University of Delaware			Budget Page No: <u>1</u>		
PRINCIPAL INVESTIGATOR/PROJECT DIRECTOR Michael Mackay			Requested Duration: <u>22</u> (Months)		
A. SENIOR PERSONNEL: PI/PD, Co-PI's, Faculty and Other Senior Associates (List each separately with title; A.6. show number in brackets)		DOE Funded Person-mos.		Funds Requested	
		CAL	ACAD	QUMR	by Applicant
1. Dr. Michael Mackay		2.00		40,074.00	
2.					
3.					
4.					
5.					
6. () OTHERS (LIST INDIVIDUALLY ON BUDGET EXPLANATION PAGE)					
7. (1) TOTAL SENIOR PERSONNEL (1-6)				40,074.00	0.00
B. OTHER PERSONNEL (SHOW NUMBERS IN BRACKETS)					
1. (1) POST DOCTORAL ASSOCIATES		22.00		78,000.00	
2. () OTHER PROFESSIONAL (TECHNICIAN, PROGRAMMER, ETC.)					
3. (1) GRADUATE STUDENTS				24,000.00	
4. () UNDERGRADUATE STUDENTS					
5. () SECRETARIAL - CLERICAL					
6. () OTHER					
TOTAL SALARIES AND WAGES (A+B)				142,074.00	0.00
C. FRINGE BENEFITS (IF CHARGED AS DIRECT COSTS)				14,585.00	
TOTAL SALARIES, WAGES AND FRINGE BENEFITS (A+B+C)				156,659.00	0.00
D. PERMANENT EQUIPMENT (LIST ITEM AND DOLLAR AMOUNT FOR EACH ITEM.)					
TOTAL PERMANENT EQUIPMENT				30,000.00	
E. TRAVEL		1. DOMESTIC (INCL. CANADA AND U.S. POSSESSIONS)		12,000.00	
		2. FOREIGN			
TOTAL TRAVEL				12,000.00	0.00
F. TRAINEE/PARTICIPANT COSTS					
1. STIPENDS (Itemize levels, types - totals on budget justification page)					
2. TUITION & FEES					
3. TRAINEE TRAVEL					
4. OTHER (fully explain on justification page)					
TOTAL PARTICIPANTS ()		TOTAL COST		0.00	0.00
G. OTHER DIRECT COSTS					
1. MATERIALS AND SUPPLIES				1,388.00	
2. PUBLICATION COSTS/DOCUMENTATION/DISSEMINATION					
3. CONSULTANT SERVICES					
4. COMPUTER (ADPE) SERVICES					
5. SUBCONTRACTS				39,155.00	
6. OTHER					
TOTAL OTHER DIRECT COSTS				40,543.00	0.00
H. TOTAL DIRECT COSTS (A THROUGH G)				239,202.00	0.00
I. INDIRECT COSTS (SPECIFY RATE AND BASE) 53% - Base 170,047					
TOTAL INDIRECT COSTS				90,125.00	
J. TOTAL DIRECT AND INDIRECT COSTS (H+I)				329,327.00	0.00
K. AMOUNT OF ANY REQUIRED COST SHARING FROM NON-FEDERAL SOURCES					
L. TOTAL COST OF PROJECT (J+K)				329,327.00	0.00

MICHAEL E. MACKAY

Professor

Department of Materials Science and Engineering

Department of Chemical Engineering (affiliated faculty member)

University of Delaware, Newark, DE 19716

phone, (302) 831-6194; fax, (302) 831-4545; email, mem@udel.edu; URL, www.nanoeverything.com

Education:

Ph.D.in Chemical Engineering, 1985, University of Illinois – Urbana-Champaign,

Advisor: Prof. A.J. McHugh, Thesis: 'Behavior of polymer solutions and melts in shearing and elongational flow using streak photography and birefringence'

M.S.in Chemical Engineering, 1983, University of Illinois – Urbana-Champaign.

Adviser: Prof. A.J. McHugh, Thesis: 'Converging flow of a Newtonian fluid in a film extrusion geometry'

B.S. in Chemical Engineering (with distinction), 1979, University of Delaware

Advisor: Prof. M.E. Paulaitis. Thesis: 'Optimal representation of vapor-liquid equilibria'

Professional Experience:

2008 – Present	Professor, University of Delaware
2001 – 2008	Professor, Michigan State University
1999 – 2001	Professor, Stevens Institute of Technology
1994 – 1998	Associate Professor, Univ. Queensland (U.S. equivalent – Professor)
Fall 1994	Visiting Professor, Univ. Delaware
1991 – 1994	Senior Lecturer, Univ. Queensland (U.S. equivalent – Associate Professor)
Fall 1990	Visiting Professor, Cambridge Univ.
1987 – 1991	Lecturer, Univ. Queensland (U.S. equivalent – Assistant Professor)
1985 – 1987	Postdoctoral Fellow, Univ. Melbourne
1979 – 1980	Staff Engineer, Procter and Gamble

Honors, Awards, Fellowships:

Society of Rheology Publication Award, 2001

Max Planck Institute. Workshop Lecturer – Colloidal Processing of Ceramics. 1998

Editorial Board – Resources, Conservation and Recycling, Elsevier

Editorial Board Resources, Conservation and Recycling, ELSEVIER
College of Engineering Teaching Award, Univ. Queensland, 1993

Exxon Graduate Fellowship, 1984
Exxon Graduate Fellowship, 1982
Chevron Graduate Fellowship, 1989
Chemical Engineering Graduate Fellowship, 1980-1981

Degree with Distinction – University of Delaware, DE
College of Engineering Teaching Fellowship, 1978

Membership in Professional and Honorary Societies:

American Institute of Chemical Engineers, Society of Rheology, American Chemical Society, American Association for the Advancement of Science, American Physical Society, Materials Research Society

Selected Publications:

Selected Publications:

1. A. Tuteja, P. M. Duxbury and M. E. Mackay, "Polymer chain swelling induced by dispersed nanoparticles," *Phys. Rev. Letters*, **100** (2008) 077801 1 - 4.
2. E. S. McGarry, A. L. Frischknecht, L. J. D. Frink and M. E. Mackay, "Surface-induced First Order Transition in Athermal Polymer/Nanoparticle Blends," *Phys Rev Letters*, **99** (2007) 238302-1 - 4.
3. R. S. Krishnan, M. E. Mackay, P. M. Duxbury, A. Pastor, C. J. Hawker, B. Van Horn, S. Asokan and M. S. Wong, "Self-assembled multilayers of nanocomponents," *Nano Letters*, **7** (2007) 484-489.
4. J. Xu, D. A. Bohnsack, M. E. Mackay and K. L. Wooley, "Unusual Mechanical Performance of Amphiphilic Crosslinked Polymer Networks," *J. Am. Chem. Soc.*, **129** (2007) 506-507.
5. A. Tuteja, M. E. Mackay, S. Narayanan, S. Asokan and M. S. Wong, "Breakdown of the continuum Stokes-Einstein relation for nanoparticle diffusion." *Nano Letters*. **7** (2007) 1276-1281.

6. M. E. Mackay, A. Tuteja, P. M. Duxbury, C. J. Hawker, B. V. Horn, Z. Guan, G. Chen and R. S. Krishnan, "General Strategies for Nanoparticle Dispersion," *Science*, **311** (2006) 1740-1743.
7. T. E. Dukette, M. E. Mackay, B. Van Horn, K. L. Wooley, E. Drockenmuller, M. Malkoch and C. J. Hawker, "Conformation of Intramolecularly Cross-Linked Polymer Nanoparticles on Solid Substrates," *Nano Letters*, **5** (2005) 1704-1709.
8. R. S. Krishnan, M. E. Mackay, C. J. Hawker and B. Van Horn, "Influence of molecular architecture on the dewetting of thin polystyrene films," *Langmuir*, **21** (2005) 5770-5776.
9. S. Sivakova, D. A. Bohnsack, M. E. Mackay, P. Suwanmala and S. J. Rowan, "Utilization of a Combination of Weak Hydrogen-Bonding Interactions and Phase Segregation to Yield Highly Thermosensitive Supramolecular Polymers," *J. Am. Chem. Soc*, **127** (2005) 18202-18211.
10. Mackay, M. E., T. T. Dao, A. Tuteja, D. L. Ho, B. van Horn, H.-C. Kim and C. J. Hawker, "Nanoscale effects leading to non-Einstein-like decrease in viscosity," *Nature Materials* **2** (2003) 762-766.

Synergistic Activities:

1. Developed a course in Nanoscale Characterization that has been taught multiple times to graduate students
2. Member of the Nanotechnology Advisory Board to BASF
3. Presented a 3 day course on Nanoscale Characterization at The University of Queensland in August 2 – 4, 2006.
4. Given presentations to elementary school children on nanotechnology several times.
5. Session chair and organizer for "Polymeric Nanostructures" session at Chicago 2007 ACS Meeting (with Prof. Stuart Rowan and Dr. Amalie Frischknecht).
6. Session chair and organizer for "Novel Flows" session at 2007 Salt Lake City AIChE Meeting (with Prof. A. Ladd)

Graduate Students, Postdoctoral Researchers and Collaborators:

Graduate students:

Ph.D (29 supervised in total)

Abdulhamid Dajan (1995) Univ. Qld.
 Peter Farrington (1995) Moldflow
 David Henson (1995) Consulting Germany
 John O'Mahony (1996) Nat. Lab. Ireland
 Babak Kaffashi (1997) Iran
 Stuart Smyth (1998) Consulting Australia
 Chen-Hua Liang (1998) Singapore
 Vince O'Brien (1998) Consulting Australia
 Stewart McGlashan (1998) Univ. Qld
 Grant Hay (1999) Brady Corp
 Justin Cooper-White (1999) Melbourne Univ.
 Mark Coghill (2001) RioTinto
 Miyoun Jeong (2003) NIST
 R.S. Krishnan (2006) Intel
 L. Passeno (2006) Sika
 A. Tuteja (2006) MIT
 M. Holmes (2007) Sandia
 T. Bohnsack (2007) Henkel
 D. Bohnsack (2007) TA Instruments

MS (2 supervised)

Glenda Carmezini (2000)

J. Sutton (2003)

Presently supervising

Erica Tseng (MSE-MSU)
 Jon Kiel (ChE-MSU)
 Jon Seppala (ChE-MSU)
 Brett Guralnick (ChE-UD)
 Jeong Jae Wie (ChE-UD)

Postdoctoral Researchers:

(8 supervised in total)

Peter Halley (1994-5) Univ. Qld.
 Camilla Kelly (1995-8) Univ. Qld.
 Eric Weisser (1996-8) National Starch
 Kailash Awati (1997-9) Consulting Germany
 Ye Hong (1998-9) Univ. Qld.
 Tien D. Dao (2001-3) Michigan State University
 Erin McGarrity (2005-present)
 Donia Friedman (2008-present)

Collaborators:

Thesis Advisors:

A.J. McHugh (Lehigh University)
 M.E. Paulaitis (Ohio State University)

Recent Collaborators:

G. Baker (MSU), P. Duxbury (MSU)
 C. Hawker (UCSB), N. Wagner (Delaware),
 M.S. Wong (Rice U), K.L. Wooley (Wash U-St. L),
 S. Rowan (CWRU), A. Frischknecht (Sandia)
 Z. Guan (UCI), T Russell (U Mass)

References

1. Krishnan, R. S., Mackay, M. E., Duxbury, P. M., Hawker, C. J., Asokan, S., Wong, M. S., Goyette, R. & P. Thiagarajan. Improved polymer thin-film wetting behavior through nanoparticle segregation to interfaces. *J. Phys.: Cond Matter* 19, 356003 (2007).
2. Krishnan, R. S., Mackay, M. E., Hawker, C. J. & Van Horn, B. Influence of molecular architecture on the dewetting of thin polystyrene films. *Langmuir* 21, 5770-5776 (2005).
3. McGarry, E. S., Frischknecht, A. L., Frink, L. J. D. & Mackay, M. E. Surface-induced First Order Transition in Athermal Polymer/Nanoparticle Blends. *Phys Rev Letters* in press (2007).
4. Holmes, M. A., Mackay, M. E. & Giunta, R. K. Nanoparticles for Dewetting Suppression of Thin Polymer Films used in Chemical Sensors. *J. Nanopart. Res.* 9, 753-763 (2007).
5. Krishnan, R. S., Mackay, M. E., Duxbury, P. M., Pastor, A., Hawker, C. J., Van Horn, B., Asokan, S. & Wong, M. S. Self-assembled multilayers of nanocomponents. *Nano Lett* 7, 484-489 (2007).
6. Decher, G. Fuzzy nanoassemblies: Toward layered polymeric multicomposites. *Science* 277, 1232-1237 (1997).
7. Krishnan, R. S., Mackay, M. E., Duxbury, P. M., Pastor, A., Hawker, C. J., Horn, B. V., Wong, M. S. & Asokan, S. Self-assembled multilayers of nanocomponents. *Nano Lett.* 7, 484-489 (2007).
8. Hariharan, A., Kumar, S. K. & Russell, T. P. Reversal Of The Isotopic Effect In The Surface Behavior Of Binary Polymer Blends. *J.Chem.Phys.* 98, 4163-4173 (1993).
9. 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).
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11. Wu, J. Z. Density functional theory for chemical engineering: From capillarity to soft materials. *AIChE J.* 52, 1169-1193 (2006).
12. Wu, J. Z. & Li, Z. D. Density-functional theory for complex fluids. *Ann. Rev. Phys. Chem.* 58, 85-112 (2007).
13. Rosenfeld, Y. Free-Energy Model for the Inhomogeneous Hard-Sphere Fluid Mixture and Density-Functional Theory of Freezing. *Phys. Rev. Lett.* 63, 980-983 (1989).
14. Tripathi, S. & Chapman, W. G. Microstructure of inhomogeneous polyatomic mixtures from a density functional formalism for atomic mixtures. *J. Chem. Phys.* 122, 094506 (2005).
15. Tripathi, S. & Chapman, W. G. Microstructure and thermodynamics of inhomogeneous polymer blends and solutions. *Phys. Rev. Lett.* 94, 087801 (2005).
16. Wertheim, M. S. Fluids with highly directional attractive forces. II. Thermodynamic perturbation theory and integral equations. *Journal of Statistical Physics* 35, 35-47 (1984).
17. Wertheim, M. S. Fluids with highly directional attractive forces. I. Statistical thermodynamics. *Journal of Statistical Physics* 35, 19-34 (1984).
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19. Roth, R., Evans, R., Lang, A. & Kahl, G. Fundamental measure theory for hard-sphere mixtures revisited: the White Bear version. *J. Phys.-Cond. Matt.* 14, 12063-12078 (2002).
20. Guan, Z., Cotts, P., McCord, E. & McLain, S. Chain Walking: A New Strategy to Control Polymer Topology. *Science* 283, 2059-2062 (1999).
21. Tuteja, A., Duxbury, P. M. & Mackay, M. E. Multifunctional nanocomposites with reduced viscosity. *Macromolecules* in press (2007).
22. Seemann, R., Herminghaus, S., Neto, C., Schlagowski, S., Podzimek, D., Konrad, R., Mantz, H. & Jacobs, K. Dynamics and structure formation in thin polymer melt films. *J Phys-Condens Mat* 17, S267-S290 (2005).
23. Israelachvili, J. N. *Intermolecular and Surface Forces* (Academic Press, New York, 1992).
24. Gupta, S., Zhang, Q. L., Emrick, T., Balazs, A. C. & Russell, T. P. Entropy-driven segregation of nanoparticles to cracks in multilayered composite polymer structures. *Nat Mater* 5, 229-233 (2006).
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26. Tuteja, A., Mackay, M. E., Narayanan, S., Asokan, S. & Wong, M. S. Breakdown of the continuum Stokes-Einstein relation for nanoparticle diffusion. *Nano Lett* 7, 1276-1281 (2007).
27. Brochard-Wyart, F. & deGennes, P. G. Viscosity at small scales in polymer melts. *Eur. Phys. J. E* 1, 93-97 (2000).
28. Xavier, J. H., Sharma, S., Seo, Y. S., Isseroff, R., Koga, T., White, H., Ulman, A., Shin, K., Satija, S. K., Sokolov, J. & Rafailovich, M. H. Effect of nanoscopic fillers on dewetting dynamics. *Macromolecules* 39, 2972-2980 (2006).