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Three-Dimensional Nanoparticle Arrays Templated by Self-Assembled Block-Copolymer Gels

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Summary: Water-soluble triblock copolymers (PEO-PPO-PEO) are utilized to provide thermoreversible micellar templates for three-dimensional nanoparticle arrays. The triblock forms a cubic micellar structure with typical dimensions of tens of nanometers. The temperature-dependent amphiphilic nature of the block copolymers provides increased structure control and allows the use of pre-made silica and gold nanoparticles as well as globular proteins. Using rheology and small-angle neutron scattering (SANS), we characterize the influence of the nanoparticles on the local particle structure and on the macroscopic mechanical properties. We are able to incorporate significant quantities of nanoparticles into the block copolymer gel without destroying the ordered structure. Contrast matching SANS demonstrates that some level of the template structure is transferred to the nanoparticles. This study demonstrates the feasibility and potential of using this simple approach to generate novel nanoparticles-polymer composites.

Keywords: block copolymers; gels; nanoparticles; rheology; SANS

Introduction

The self-assembly of block-copolymers in a selective solvent is used to drive the organization of dispersed nanoparticles into arrays with three-dimensional periodicity. Amphiphilic block-copolymers form lyotropic and thermotropic mesophases with lattice periodicity on the nanometer length-scale and order that persists over macroscopic distances. These self-organized polymer mesophases are used as templates to drive the organization of nanoparticulate materials with sizes on the length-scale of the crystal lattice. The variety of 1D (lamellae), 2D (hexagonal cylinders) and 3D (cubic and bicontinuous cubic) crystal phases that have been observed in block-copolymers allow for the design of well-organized nanocomposite materials[1]. Previous studies have shown that small molecule surfactants can also be used to template nanoparticles[2].

We are quantifying the transfer of structure and the influence of nanoparticle additives on the macroscopic properties of nanocomposites based on thermoreversible block copolymers. Water-soluble poly (ethylene oxide) PEO and poly (propylene oxide) PPO tri-

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block copolymers commonly known as Pluronics® were chosen as a template materials. These polymers have been widely studied[1][3] and their phase behavior has been characterized. The reversible gelation (gel formation on increasing temperature) arises from a difference in dehydration temperatures between the middle PPO block and the two PEO end blocks. This drives the formation of micelles that have a dehydrated PPO core and an extended and hydrated PEO corona. At sufficiently high polymer concentrations, the polymer micelles pack into crystals with long range order. The water solubility, low toxicity of the polymer and the fact that the temperature-dependent phase transition occurs at temperatures in the 5-40°C range, has fueled interest for use in controlled drug delivery[4] and biomolecule separation[5] applications.

The thermoreversible gelation found in PEO-PPO-PEO tri-block copolymers provides significant advantages over other nanoparticle templating methods. Since samples are fluid at low temperatures, we are able to homogeneously disperse pre-manufactured nanoparticles in significant concentrations without compromising particle stability in solution. The temperature is then increased and as the micellar crystal forms around the particles, excluded volume interactions drive the 3D organization of the hydrophilic nanoparticles. This process is shown schematically in Figure 1.

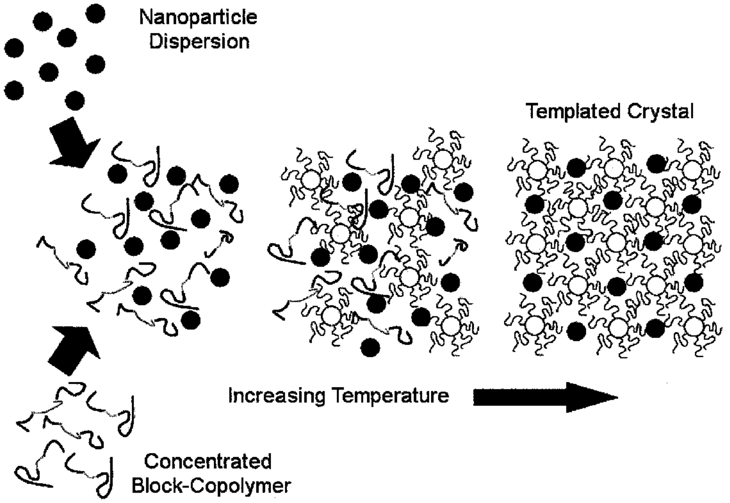

Figure 1. Schematic showing the preparation of the nanocomposites and the thermoreversible formation of the cubic crystal template.

Here we highlight some results obtained using gels containing 25w% Pluronic® F127 ($PEO_{99}PPO_{69}PEO_{99}$) in the continuous matrix. The neat polymer template at this concentration forms an FCC cubic crystal gel of micelles with a nearest neighbor distance of 22 nm[1][5].

The increased control over nanoparticle composition and concentration greatly enhances the applicability of this templating method to a large variety of nanoparticulate systems. This is an essential element in the development of applications that require the dispersion of particles that cannot be synthesized inside the template. We have been able to use this process to form nanocomposites containing relatively large quantities (1-10 w%) of different hydrophilic nanoparticles including silica nanoparticles, monolayer-protected gold clusters and bovine serum albumin (BSA). Scattering experiments confirm that dispersions of these particles without polymer do not form any ordered structures. In the absence of a template, the formation of colloidal crystals typically requires larger, monodisperse particles (> 100 nm) at higher volume fractions (> 0.5). Figure 2 shows examples of a variety of nanocomposites which are all clearly stiff gels with optical properties that depend on the nature and amount of added nanoparticles.

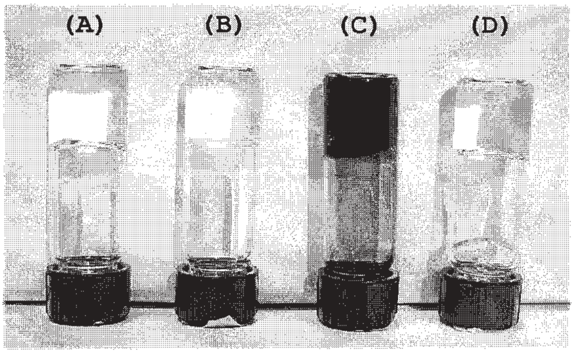

Figure 2. Image of inverted sample jars of 25 w% F127 neat polymer gel (A) and nanocomposite gels containing 25 w% F127 and 5 w% silica nanoparticles (B), 2 w% monolayer-protected gold clusters (C) and 3 w% BSA (D).

Transmission of order to nanoparticles

Small-angle neutron scattering (SANS) is utilized to evaluate the transmission of order from the template to 7 nm diameter silica nanoparticles (Ludox SM). SANS provides a direct assessment of the three-dimensional structure in a bulk macroscopic sample (rather than thin films). SANS also allows for the use of contrast-matching techniques to independently evaluate the structure of the micelle crystal and the dispersed nanoparticles.

In the contrast-matching technique the isotope ratio of atoms in the solvent is changed so that the scattering length density (SLD) of the solvent matches that of one of the dispersed materials (polymer or nanoparticles). At this contrast condition the scattering from the contrast-matched material becomes negligible and the scattering curve is dominated by the second component. This effect can be seen by examining the generalized scattering intensity equation for a two component system. In equation 1, Q is the scattering vector, ρ is the scattering length density, $I_{11}(Q)$ and $I_{22}(Q)$ represent the scattering contribution from the pure components while $I_{12}(Q)$ is the intensity contribution from cross correlations,

$$I(Q) = (\rho_1 - \rho_s)^2 I_{11}(Q) + (\rho_2 - \rho_s)^2 I_{22}(Q) + 2(\rho_1 - \rho_s)(\rho_2 - \rho_s) I_{12}(Q) \quad (1)$$

$$I(Q) = (\rho_2 - \rho_s)^2 I_{22}(Q) \quad for\ \rho_s = \rho_1 .$$

The first and last term of the equation become negligibly small as ρ_S is matched to ρ_l by changing the relative isotope composition. At 15% D_2O and 85% H_2O the SLD of the solvent is closely matched to the average SLD of the polymer micelles and the scattering intensity is dominated by the silica particles. At 58% D_2O and 42% H_2O the silica particles are matched and the scattering signal is due to the polymer micelles. Contrast matching conditions were verified with scattering experiments from the pure components.

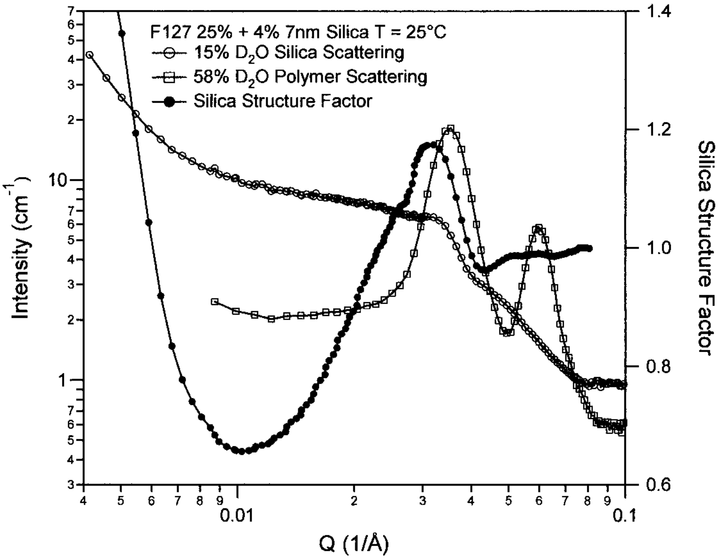

Figure 3. SANS profiles of the polymer micelles (□) and silica particles (○) for a nanocomposite containing 25 w% F127 and 4 w% silica. Also shown is the calculated structure factor (●) of the silica nanoparticles.

The scattering arising from the polymer component of the nanocomposite is characteristic of the SANS profiles that have been previously reported for these cubic crystals[1][5][6][7]. Two Bragg diffraction peaks and a small shoulder are observed that are characteristic of close packed cubic crystals. This result indicates that the addition of nanoparticles does not prevent the formation of the micelle cubic crystal and that its structure is maintained. The figure also includes the scattering intensity arising from the silica nanoparticles. The curve shows an increased scattering intensity at low Q values which indicates that phase separation of particle-poor and particle-rich regions is occurring. Further optical and rheological observations made on these nanocomposites are also consistent with this phase separation and will be discussed in detail elsewhere[8].

The scattered intensity for systems containing particles can be divided into two components, as shown in equation 2. The form factor, P(Q), arises from the shape of the particle, while the structure factor, S(Q), from the interparticle spatial correlations,

$$I(Q) = N(\rho - \rho_S)^2 V^2 \cdot S(Q) \cdot P(Q). \qquad (2)$$

In equation 2, $(\rho-\rho_S)$ is the particle scattering contrast, N is the number of particles and V is the particle volume. The form factor is measured directly by collecting scattering curves for samples with negligible interparticle correlations (dilute or unstructured dispersions) where S(Q) = 1. The structure factor on concentrated interacting samples is then calculated by correcting the data using the measured P(Q) and the known concentrations. Figure 3 shows the calculated silica structure factor that arises from the order transferred by the micelle cubic crystal to the nanoparticles. The peak in the silica structure factor occurs at a similar characteristic length scale ($D=2\pi/Q$) as the first Bragg diffraction peak from the micelle cubic crystal. This is a clear indication that some of the template order is being transferred to the silica particles. However, the structure factor peak is broader than the polymer peak and it is shifted towards a larger characteristic length scale (smaller Q values). Although, the scattering data validates the templating process it also shows that the nanoparticle crystals are not perfect. This is likely due to the mobility of nanoparticles in the interstitial spaces and the fact that the micelle template itself is not a perfect crystal. Additionally, large incoherent background levels and limited experimental resolution, prevent clear observation of higher order peaks. Therefore the full crystal structure of the nanoparticles cannot be identified. Still, we expect that nanoparticles located in the octahedral interstitial sites of the micelle crystal will form an FCC crystal with the same periodicity and orientation. These initial results indicate that spatial order is transferred from the template to the imbedded nanoparticles. We hope that improved templating can be achieved through shear orientation, or by manipulating the relative concentration and relative size of the components.

Additive effect on the mechanical properties

The addition of nanoparticles to the micelle cubic crystals has a direct effect on the macroscopic properties of the final nanocomposites. Figure 4 shows the change in modulus with temperature for nanocomposite samples made by addition of 7nm silica nanoparticles to F127 dispersions at three different concentrations. The neat polymer samples (closed symbols) form gels on increasing temperature that reach a maximum in complex modulus (G^*) at temperatures above 40°C. Rheological studies on the neat micelle cubic crystals have been previously reported and show similar results[7][9-11].

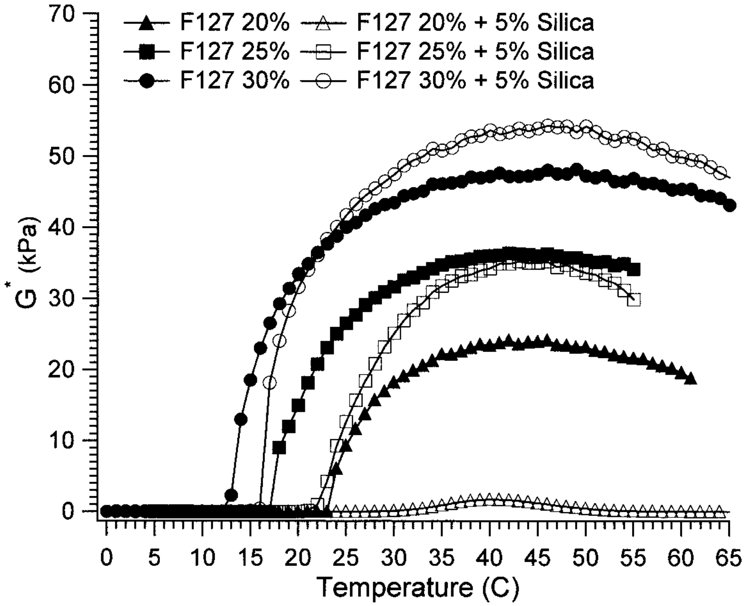

Figure 4. Complex modulus (G^*) of neat Pluronic® F127 (closed symbols) and the corresponding nanocomposites containing 5w% silica nanoparticles (open symbols).

The addition of 5w% silica nanoparticles has a direct effect on the complex modulus of the nanocomposite gels (open symbols). The effect of the nanoparticle additives changes depending on the concentration of polymer in the matrix. When the concentration of polymer is 20w% F127, the addition of nanoparticles causes a significant drop in the modulus and the resulting nanocomposite is much weaker than the corresponding neat matrix. At a concentration of 25w% F127, the addition of nanoparticles also results in weaker gels at temperatures just above the gel temperature, but both the filled and neat matrix show the same mechanical behavior at temperatures near 45°C. When the polymer concentration is 30w% F127, the nanocomposite actually has a higher complex modulus than the neat matrix at temperatures above 20°C. These changes in variable macroscopic properties must be considered in development of nanocomposites for specific applications. The influence of relative size, nanoparticle concentration and thermal history has also been evaluated and is reported elsewhere[8].

Conclusion

Nanoparticle arrays with three-dimensional order are formed through the transfer of structure from a self-assembled micelle crystal template. The thermoreversibility of the micelle crystals enables the use of pre-manufactured particles that are dispersed at low temperatures. When the temperature is increased, the cubic crystal template forms around the particles and order is transferred. The success of this templating method is demonstrated through contrast-matched SANS experiments. The additives have a significant influence on the rheological properties of the gels but do not prevent the formation of the cubic crystal. While the parameter space of this templating method is large, the increased number of degrees of freedom will allow for versatility in nanocomposite design for emerging applications.

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