Bimodality and Re-entrant Behaviour in Hierarchical Self-Assembly of Polymeric Nanoparticles

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I. SYNTHESIS

Polystyrene grafted Gold Nanoparticles (PGNPs) are synthesized by one phase 'grafting to' method^{1,2}. Thiol terminated Polystyrene (96 μ M, 22ml) solution in Tetrahydrofuran (THF) is stirred overnight. Gold(III) Chloride trihydrate (12mM, 2ml) solution in THF is mixed to it and continued stirring for 1 hour. The reduction of Gold(III) Chloride trihydrate is triggered by adding Superhydride (0.5M, 600 μ l) drop by drop to the stirring mixture kept in icebath. After 2 hours of stirring, a few milliliters of ethanol is added and the mixture is centrifuged to precipitate the nanoparticles. The supernatant is discarded and nanoparticles are redissolved in THF-ethanol mixture. It is centrifuged again, and the process is repeated for a few times in order to remove all the ungrafted polymer chains. The final precipitate is dissolved in chloroform and dried under vacuum for overnight to yield powder.

II. CHARACTERIZATION OF PGNPS

Gold nano core size of PGNPs is measured using Transmission Electron Microscopy for which the grid is prepared by drop casting PGNP solutions of concentration ~ 0.25mg/ml. TEM images of PGNPs are shown in figure 1 and histograms of the core diameter which are estimated using sigma scan-pro software are provided in the insets. Gaussian fitting is carried out to extract prominent diameter and polydispersity of core size. The diameters are estimated as $3.1 \pm 0.6nm$ and 3.1 ± 0.5 for PGNP-53K and PGNP-3K respectively.



FIG. 1. TEM images of PGNP53K (panel:a, scalebar:20nm) and PGNP3K (panel:b, scalebar:10nm). Insets show the histograms and the Gaussian fits.

Quantification of the number of polymer chains grafted onto single gold nano-core (functionality) is done using Thermo Gravimetric Analysis (TGA). Continuous weight loss curves of PGNPs on heating are shown in figure 2, where residual weight is taken as the weight of gold (W_{Au}) and the difference from the net weight is taken as the weight of PST (W_{PST}). Functionality is calculated using the formula,

$$f = \frac{W_{PST}}{W_{Au}} \frac{4\pi r_c^3}{3} \frac{\rho_{Au} N_A}{M_w},\tag{1}$$

where r_c is the core radius, ρ_{Au} (= 19.3 g/cm^3) is the density of gold, N_A is the Avogadro number and M_w is the molecular weight of grafted polystyrene. Functionality, calculated for PGNP-53K is 30 and that for PGNP-3K is 40.



FIG. 2. TGA curves (a) PGNP-53K and (b) PGNP-3K.

The Hydrodynamic radius, R_h is estimated by employing Dynamic Light Scattering (DLS) technique. The correlation functions of PGNPs are plotted in figure3a. The vertical axis in figure 3a represents the correlation function of the scattered intensity, $g(\tau) = 1 + A \exp(-2Dq^2t)$ where A is the intercept of the correlation function, D is diffusion coefficient and $q = (4\pi n/\lambda) \sin(\theta/2)$ is the scattering vector, defined by the refractive index (*n*), the wavelength of the laser (λ) and the scattering angle (θ). The hydrodynamic radius is estimated using the Stokes-Einstein relation, $R_H = k_B T/6\pi\eta D$, where k_B is the Boltzmann constant, T is temperature and η is viscosity as 27*nm* (PGNP53K) and 8*nm* (PGNP3K).

The effective size of PGNPs in melt (d_{melt}) is expected to be much smaller than R_H , since the grafted polymers are in different chain conformation. As mentioned in the main manuscript, this estimates of d_{melt} could be less than the actual value due to chain interpenetration between neighbouring PGNPs. Small Angle X-ray Scattering (SAXS) is used for the measurement of melt



FIG. 3. a) Correlation function vs time obtained from DLS, PGNP53K (○) and PGNP3K (□). SAXS data of b) PGNP53K and c) PGNP3K.

diameter of PGNPs. Figure 3b,c show the scattering intensity, I(q) as a function of scattering vector (q). Intensity displays a prominent peak at a specific scattering vector which corresponds to the melt diameter, as $d_{melt} = \frac{2\pi}{q}$. The estimated values of d_{melt} are 17*nm* (PGNP-53K) and 7.4*nm* (PGNP-3K).

III. METHOD OF FILM TRANSFER

The PGNP film formed on the water surface is compressed by moving the LB barrier with a speed of 5mm/min and surface pressure is measured using a Wilhelmy plate. At a surface pressure of 5mN/m, the compression is stopped and the film is transferred to the glass substrate by with-drawing the substrate, vertically, from the water subphase through the PGNP layer with a speed of 0.5mm/min, to avoid distortion of this layer morphology formed on water. The temperature of the LB water subphase was maintained at $25^{\circ}C$ during the entire process.

IV. THIN FILM PATTERNS OF PGNP53K

Figure 4 shows the AFM images for PGNP53K solutions where similar variation in the length scale of patterns, as for the PGNP3K case, can be observed on increasing the concentration. Two dimensional patterns show a change from long to short wavelengths with increase in the concentration and again enter back to long wavelengths at high concentrations.



FIG. 4. AFM images of films prepared from PGNP53K solutions of concentrations (a) 0.05mg/ml; (b) 0.5mg/ml; (c) 1.5mg/ml; (d) 3mg/ml.



V. EFFECT OF TRANSFER SURFACE PRESSURE ON PATTERNS

FIG. 5. AFM images of PGNP-53K film transferred at surface pressures a) 0.5mN/m and b)10mN/m

We confirm that there is no effect of compression on the morphology for a range of surface pressures (0-10mN/m). Figure 5 shows AFM images of films of PGNP-53K (concentration 0.15mg/ml) transferred at 0.5mN/m and 10mN/m which exhibit similar features in the morphology. The experiments presented in this study were obtained at a surface pressure of 5mN/m and aren't affected by the compression. The pressure has been essentially used to assist transfer of the patterns from the water surface to the glass substrate.

VI. DETAILS OF THE THIN FILM MODELLING

In the modelling approach for the thin film of polymer solution, we investigate the coupled evolution of the film height and the polymer concentration within the thin film (vertically averaged). The basic ingredients of the coupled evolution equations are the mobilities (coming from hydrodynamics) and the energies (coming from equilibrium statistical physics). The wetting energy of the thin film is given by the van der Waals potential^{3,4},

$$f(h,\phi) = \frac{-A(\phi)}{2h^2} + \frac{B}{8h^8},$$
(2)

where the effective Hamaker constant of the polymer solution, $A(\phi)$ is calculated from the optical indices of solvent and solute employing Lifshitz theory within the effective medium approximation⁵ and *B* is the coefficient of the short-range interaction. Hamaker constant, $A(\phi)$ of polystyrene-chloroform solution exhibit a linear variation with concentration ϕ as shown in figure 6, for which a linear fit, $A(\phi) = A_0(1 + M_1\phi)$ gives $A_0 = 1.08 \times 10^{-20}$ Joules and $M_1 = 1.34$.



FIG. 6. Variation of Hamaker constant of polystyrene-chloroform solution with concentration. Linear fit $(A(\phi) = A_0(1 + M_1\phi))$ is also shown.

For the linear stability analysis of the evolution equation, all parameters are taken to be that of polystyrene-chloroform system. The hydrodynamic radius is that of polystyrene-3K in chloroform, $R_h = 1.1$ nm, monomer size of styrene a = 0.3nm and the range of energetic interactions between monomers is $r_0 \sim a$. Viscosity⁶ and interface tension³ of the solution are assumed to be that of the solvent (chloroform), $\eta = 0.5 cp$ and $\gamma = 27.5 mN/m$. The concentration is chosen as 0.1, which is in the range of concentrations explored in experiments. The Flory interaction parameter χ is assumed to be in the range of values that are found for PS at the extreme solvent qualities of the present system, i.e., PS in chloroform (0.4) and PS in water (4).

The film thickness in most of our analysis is chosen as 30*nm*, for which the reason is the following: After the suspension film is brought onto the substrate layer, it first evolves by homogeneous evaporation of the chloroform. Although the involved thick films might already be unstable w.r.t. the various lateral instabilities, the involved typical timescales are much too large to



FIG. 7. Dispersion curves of PS3K for concentrations 0.01(I), 0.1(II), 0.2(III), 0.5(IV) at $\chi = 0.73$ and h = 50nm.

affect the process (they are much larger than the evaporation timescale). However, when the film thickness reaches about 20 - 50nm through homogeneous evaporation, the dewetting timescales have sufficiently strongly decreased (i.e., the growth rates of the instability has increased) as they typically depend on the film height via a power law⁷. Hence, the height of the polymer solution thin film is fixed at h = 30nm, a value (well inside the relevant mesoscopic range of 20 - 50nm) where the growth rates of the instabilities dominate evaporation and the instability proceeds quasi-instantaneously as compared to evaporation. In figure 7, we show the dispersion curves for four different concentrations at $\chi = 0.73$ at a larger thickness h = 50nm. It implies that the nature of instabilities at various concentrations, i.e., the transition of the dominating instability from dewetting to decomposition and re-entrance to dewetting are essentially the same.

Linear stability analysis predicts the existence of both, dewetting instability and decompositional instability at intermediate concentrations. As they have strongly different dominant wavenumbers their growth gives rise to bimodality. However, the growth rates vary with χ and ϕ as shown in figure 8. With increasing χ , the growth rate of the small length scale mode can significantly dominate resulting in a weaker growth of the large length scale pattern, i.e., in a weaker modulation of the small scale structure on the large length scale.

Experimentally, we have observed bimodality in a specific parameter range. An example is shown in figure 9. Figure 9a shows a $10\mu m \times 10\mu m$ AFM image of PGNP53K film prepared from 0.25mg/ml solution, for which the power spectral density shows a peak at ~ $1\mu m$ and visual



FIG. 8. Ratios of maximum growth rates of compositional instability (β_{ϕ}) and dewetting instability (β_{h}) for PS3K, (a) variation with Flory parameter χ at h = 30nm and $\phi = 0.1$; (b) variation with concentration ϕ at h = 30nm and $\chi = 0.73$. The lines indicate where the growth rates of both instabilities are equal.



FIG. 9. (a) $10\mu m \times 10\mu m$ AFM image of PGNP53K film which shows the long-wave dewetting structure as hole pattern. Inset shows the corresponding power spectral density. (b) $2\mu m \times 2\mu m$ AFM image showing smaller length scale structures ('yellow blobs').

inspection shows a network-like structure. The small area scan image $(2\mu m \times 2\mu m)$ in figure 9b shows the presence of shorter length scale modes in the pattern, namely, arrangements of clusters ('yellow blobs') that themselves consist of many particles.

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