Electronic Supplementary Material (ESI) for Soft Matter.

Supporting Information

Nanorod Aspect Ratio Controls the Dispersion, Local Orientation, and Optical Absorption of Polymer Nanocomposite Films

Dongliang Wang[a,b] *Michael J. A. Hore* [c] *Xingchen Ye,*[d] *Chen Zheng,*[a,b] *Christopher B. Murray,*[a,b,d] *Russell J. Composto*[a,b,*]

[a] Department of Materials Science and Engineering, University of Pennsylvania, Philadelphia, PA 19104, United States.

[b] Laboratory for Research on the Structure of Matter, Philadelphia, PA 19104, United States.

[c] National Institute of Standards and Technology, Center for Neutron Research, Gaithersburg, MD, United States.

[d] Department of Chemistry, University of Pennsylvania, Philadelphia, PA 19104, United States.

* Corresponding author: composto@seas.upenn.edu

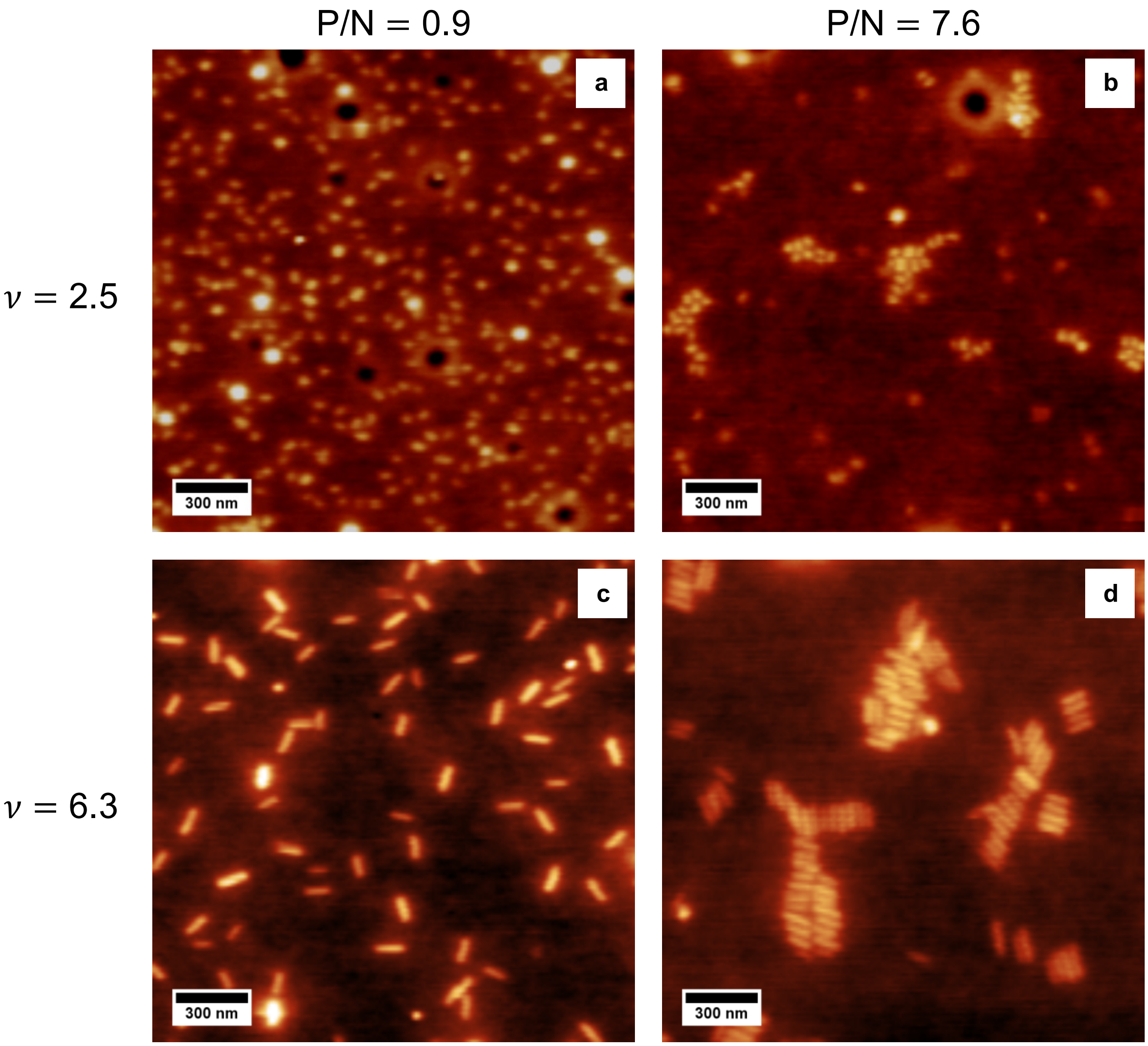

Figure S1. AFM topography images of PS-Au NRs in PS films for ν = (a, b) 2.5 and (c, d) 6.3. The left column shows that the PS-Au NRs are dispersed for $P/N = 0.9$, whereas the right column shows the aggregation of PS-Au NRs for $P/N = 7.6$. The Au NRs volume fraction is about 5 %. The z-scale is 6 nm in all images.

Nanorod Morphology: Comparison of AFM and SEM.

To complement SEM analysis, AFM is performed and topography images are shown in Figure S1. Because AFM was previously used to characterize the $\nu = 3.3$ system, only the images for the $\nu = 2.5$ and 6.3 systems are included in Figure S1. As in Figure 1, the left and right columns correspond to $P/N = 0.9$ (*i.e.*, wet brush) and 7.6 (*i.e.*, dry brush), respectively. The bright (higher) regions correspond to isolated nanorods in Figure S1a and S1c, and mixtures of isolated and aggregated nanorods in Figures S1b and S1d within the film. Qualitatively, the Au NR morphology is consistent with that obtained from SEM micrographs in Figure 1. Note that tapping mode AFM may yield larger height variations than the actual topography due to different tip-surface interactions above the Au NRs versus those far from the NRs. Nevertheless, because the height difference between the discrete bright areas and continuous dark region is much less, ≈ 5 nm, than the NR diameter (15 nm), the topography images indicate that the Au NRs are located beneath the surface. In a previous study of polystyrene-grafted gold nanospheres, Kim and Green[37] observed a slight enrichment of nanospheres at the free surface of a polystyrene film after spin coating, which may be due, in part, to autophobic dewetting between the brush and the matrix polymer. Nanosphere enrichment was also observed at the substrate due to solvent evaporation during spin coating; this behavior was also observed for drop cast films of polystyrene-*b*-poly(methyl methacrylate) containing Au NRs.[16] Thus, while the detection of small protrusions at the surface, caused by the Au NRs, may be attributed in part to an enrichment of nanorods near the free surface, the appearance of these features for both dispersed and aggregated nanorods at $P/N = 0.9$ and 7.6 suggests that they are likely due to the similarity between film thickness and nanorod diameter.

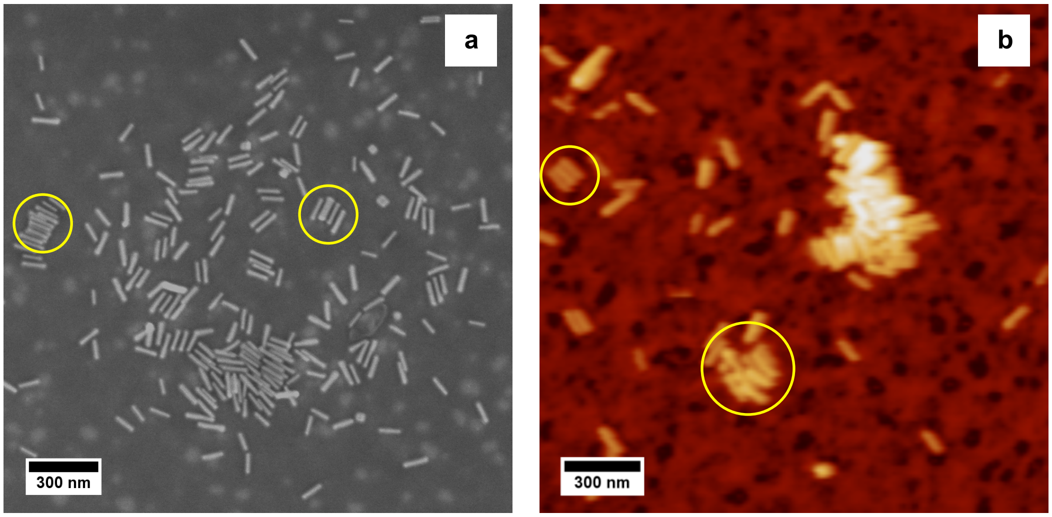

Figure S2. SEM (a) and AFM (b) images of PS-Au NRs/PS films spin cast from a solvent (cyclohexane) slightly below the Θ-Temperature (~25 ℃). The nanorods have $\nu = 6.3$ with $P/N = 7.6$. The SEM and AFM image are shown at the same magnification.

Nanorod Morphology: Effect of Spin Casting Solvent.

The effect of solvent quality on the equilibrium spacing between nanorods within aggregates was investigated by spin coating films from cyclohexane at approximately 25 ℃, which is near the theta temperature (34 °C) of polystyrene.[1] The nanorod morphology could then be compared with films cast from a good solvent, toluene, used in the prior morphology studies (*e.g.*, Figures 1 and 2). Figure S2 shows SEM (Figure S2a) and AFM (Figure S2b) images of PS(N)-Au NRs ($\nu = 6.3$) spin cast from 1.0 wt % solution of PS ($P/N = 7.6$) in cyclohexane. As in the good solvent case (*i.e.*, spin coating from a PS/toluene solution), the Au NRs aggregate in clusters due to depletion-attraction interactions between the nanorods. A comparison of Figures 1f with Figures S2a and S2b, shows that the nanorods are more disordered when spin cast from cyclohexane. While some nanorods assemble side-by-side in small clusters (yellow circles), the orientation of the nanorods is more random. The 2D orientational order parameter,

S_{avg}, for cyclohexane is 0.49, suggesting that although many nanorods are locally oriented, more disorder is found in the systems prepared from cyclohexane versus toluene. Compared to the toluene case (Figure 1f), Figure S2a shows that the nanorods appear closer to one another when spin cast from cyclohexane, suggesting that solvent quality can influence the spacing between nanorods confined within a polymer film.

Because aggregates in the cyclohexane case are not as well defined as those found in toluene, the spacing between nanorods could only be estimated from the more clearly defined aggregates such as those indicated by the yellow circles in Figure S2b. When cast from cyclohexane, the average spacing between Au NRs is $r_{avg} = 26.1$ nm, which is 10 nm smaller than that found in toluene ($r_{avg} = 36$ nm). This decrease in r_{avg} can be attributed to a thinner PS brush in cyclohexane, which is a nearly neutral solvent at 25°C. Specifically, whereas toluene swells the PS brush, the brush is less extended in cyclohexane.[2-5] Because of the rapid evaporation of the solvent during spin coating, the brushes appear to retain their height when frozen in the glassy state.[5,6] In general, the radius of gyration of an ideal chain scales as $R_g{\sim}N^{0.5}$ in a theta solvent, whereas polymer chains in a good solvent scale as $R_g{\sim}N^{0.588}$. Hence, for polymer brushes in the mushroom regime, R_g is approximately 60 % less in cyclohexane than toluene. Experimentally, the spacing between nanorods cast from cyclohexane is 72 % of that observed in toluene. Given the many simplifications, this agreement between the predicted and measured decrease in spacing is very good. While other factors are important, solvent quality appears to play a significant role in determining the separation between nanorods. These results suggest that optical properties, such as scattering and absorption, can be tuned by

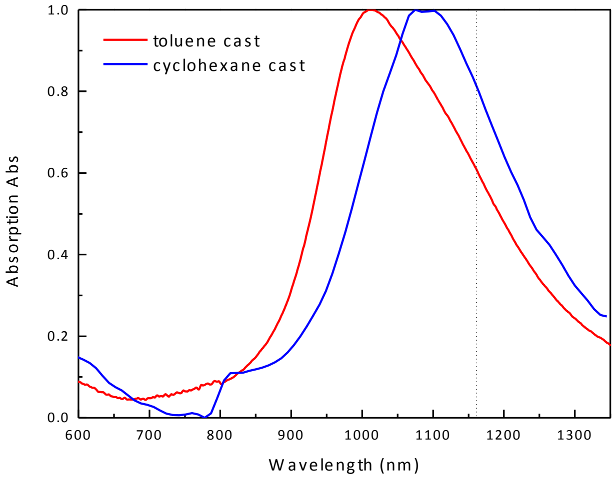

Figure S3. UV-vis spectra of PS-Au NRs spin cast from 1.0 wt % of PS in a theta solvent (cyclohexane) under room temperature (~25 ℃) comparing with in a good solvent (toluene). The nanorods $v = 6.3$ with $P/N = 7.6$. The dashed line is the LSPR wavelength for isolated Au NRs in PS. An increasing blue-shift can be observed as a solvent change from cyclohexane to toluene.

casting films from different solvents. This approach is simple compared to the alternative, namely grafting the nanorods with brushes having different values of N.

A previous study by Hore *et al.* demonstrated that the brush thickness on the nanorod surface determines the spacing between nanorods upon aggregation, which in turn affects the position of the LSPR peak.[7] For example, a larger spacing between adjacent Au NRs results in a smaller blue shift of the LSPR peak. In Figure S3, UV-vis spectra for nanocomposites are presented for two values of r_{avg}. Whereas previous work[7] varied r_{avg} by changing the degree of polymerization of the brush, N, here, r_{avg} is varied by controlling the quality of the solvent in the spin coating solution. By changing from a good solvent for the polystyrene brush (toluene) to one that is a slightly poor solvent (cyclohexane at 25 ℃), the average nanorod spacing decreases from $r_{avg} = 36$ nm to 26 nm, respectively. A significant blue shift in LSPR peak (blue line), compared to dispersed nanorods (dotted line), is detected for the film spin cast from cyclohexane, which implies that clusters contain side-by-side aligned Au NRs. However, this blue shift is not as large in magnitude as that measured from nominally the same nanocomposite prepared from toluene (red line). Whereas the smaller nanorod separation measured for films cast from cyclohexane should result in a larger blue shift relative to toluene, the clusters in these nanocomposites have a much lower degree of local orientation, with a larger range of orientation angles between adjacent particles. This difference is quantified by a comparison between orientational order parameters which are 0.49 and 0.73 for the cyclohexane and toluene cases, respectively. As a consequence, the resulting UV-vis spectrum for the cyclohexane system contains contributions from isolated nanorods, blue shifts from side-by-side aggregated nanorods, red shifts from end-to-end aligned nanorods, and similar contributions from other random orientated nanorods. While the net effect of these contributions is a blue shift of the LSPR relative to that of isolated Au NRs, the lower degree of orientational order within the clusters of aggregated nanorods reduces the magnitude of the shift.

References

1. Orwoll, R. A. Polymer-Solvent Interaction Parameter Chi. *Rubber Chem. Technol.* **1977**, *50*, 451−479.
2. Raegen, A.; Chowdhury, M.; Calers, C.; Schmatulla, A.; Steiner, U.; Reiter, G. Aging of Thin Polymer Films Cast from a Near-Theta Solvent. *Phys. Rev. Lett.* **2010**, *105*, 227801.
3. Thomas, K. R.; Chenneviere, A.; Reiter, G.; Steiner, U. Nonequilibrium Behavior of Thin Polymer Films. *Phys. Rev. Lett.* **2011**, *83*, 021804.
4. Li, R. N.; Clough, A.; Yang, Z.; Tsui, O. K. C. Equilibration of Polymer Films Cast from Solutions with Different Solvent Qualities. *Macromolecules* **2012**, *45*, 1085–1089.

5. McKenna, G.B. Size and Confinement Effects in Glass Forming Liquids: Perspectives on Bulk and Nano-Scale Behaviours. *J. Phys. IV* **2000**, *10*, *53–57*.
6. Kim, S.H.; Misner, M. J.; Xu, T.; Kimura, M.; Russell, T. P. Highly Oriented and Ordered Arrays from Block Copolymers via Solvent Evaporation. *Adv. Mater.* **2004**, *16*, 226–231.
7. Hore, M. J. A.; Frischknecht, A. L.; Composto, R. J. Nanorod Assemblies in Polymer Films and Their Dispersion-Dependent Optical Properties. *ACS Macro Lett.* **2012**, *1*, 115–121.