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## Confined Pattern-Directed Assembly of Polymer-Grafted Nanoparticles in a Phase Separating Blend with a Homopolymer Matrix

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SCHOLARONE<sup>™</sup> Manuscripts Confined Pattern-Directed Assembly of Polymer-Grafted Nanoparticles in a Phase Separating Blend with a Homopolymer Matrix

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Abstract: The controlled organization of nanoparticle (NP) constituents into superstructures of well-defined shape, composition and connectivity represents a continuing challenge in the development of novel hybrid materials for many technological applications. We show that the phase separation of polymer-tethered nanoparticles immersed in a chemically different polymer matrix provides an effective and scalable method for fabricating defined submicron-sized amorphous NP domains in melt polymer thin films. We investigate this phenomenon with a view towards understanding and controlling the phase separation process through directed nanoparticle assembly. In particular, we consider isothermally annealed thin films of polystyrene-grafted gold nanoparticles (AuPS) dispersed in a poly(methyl methacrylate) (PMMA) matrix. Classic binary polymer blend phase separation related morphology transitions, from discrete AuPS domains to bicontinuous to inverse domain structure with increasing nanoparticle composition is observed, yet the kinetics of the AuPS/PMMA polymer blends system exhibit unique features compared to the parent PS/PMMA homopolymer blend. We further illustrate how to pattern-align the phase-separated AuPS nanoparticle domain shape, size and location through the imposition of a simple and novel external symmetry-breaking perturbation via softlithography. Specifically, submicron-sized topographically patterned elastomer confinement is introduced to direct the nanoparticles into kinetically controlled long-range ordered domains, having a dense yet well-dispersed distribution of non-crystallizing nanoparticles. The simplicity, versatility and roll-to-roll adaptability of this novel method for controlled nanoparticle assembly should make it useful in creating desirable patterned nanoparticle domains for a variety of functional materials and applications.

**Keywords:** polymer nanocomposites, nanoparticles, phase separation, pattern directed assembly, symmetry breaking, confinement, ultrathin blend films



Pattern-Directed Assembly of Nanoparticles in Phase Separating Blends of Polymer-Grafted Nanoparticles in a Homopolymer Matrix

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The ability to augment the properties of polymer materials by means of nanoparticle (NP) additives has rendered polymer-matrix nanocomposites one of the most active areas in the field of polymer materials. Since the macroscopic properties of polymer nanocomposites (PNCs) sensitively depend on the morphology of the particle dispersion, one emphasis of research in the field has been to understand the governing parameters that control microstructure formation in polymer nanocomposites.<sup>1-4</sup>

For polymer grafted nanoparticles embedded in a chemically similar polymer matrix ('athermal' blend), the particle dispersion-aggregation transition is governed by the free polymer chain penetration extent into the grafted brush, or the so-called 'wetting-dewetting' transition, where 'wetting' promotes NP dispersion.<sup>5,6</sup> The final microstructures of the polymer nanocomposites are determined by the combination of nanoparticle size, grafting density, and the relative chain length of the grafts to the free polymer chains.<sup>2,7</sup> It has been shown that balancing of particle-particle and particle-matrix interactions (for example, by tailoring of the grafting density of polymer-tethered particles) enables the autonomous organization of particles into thermodynamically stable anisotropic superstructures.<sup>8</sup> Additional enthalpic interactions between the grafts and the polymer matrix have been exploited to promote nanoparticle dispersion, as demonstrated by the improved miscibility of grafted NPs in a chemically dissimilar polymer matrix where there are favorable graft-matrix enthalpic interactions.<sup>9</sup> In this case, the dispersion-aggregation transition of nanoparticles is distinct from the 'wetting-dewetting' transition.<sup>10</sup>

To harness the benefits of the 'programmed assembly' of particle fillers, methodologies have to be developed to not only control the 'shape' of individual particle aggregate, but also the spatial organization of particles within the composite material. Towards that end, nanoparticles have been organized by various templates including self-assembled block copolymers,<sup>11-13</sup>

phase-separated polymer blends,<sup>14,15</sup> and surface-bound organic templates<sup>16,17</sup>. The selective affinity of NP constituents with the template material serves to direct particle spatial organization.

In this paper, we introduce a new strategy to generate controlled nanoparticle spatial organization in a simple binary system while retaining the individual particle properties, which is aided by the unfavorable enthalpic interactions between the polymer end-grafted to the nanoparticles and the polymer matrix. This thin film system ( $\approx$  90 nm) is composed of gold nanoparticles with densely grafted polystyrene (PS,  $M_{n,PS} = 11.5$  kg / mol) ligands (hereafter denoted as AuPS) in a poly(methyl methacrylate) (PMMA,  $M_{n,PMMA} = 3.1$  kg/mol) homopolymer matrix. The average radius of the gold core (R<sub>0</sub>) is 1.21 nm and the PS grafting density ( $\sigma$ ) is 0.7 chains / nm<sup>2</sup>.

We demonstrate that the unfavorable enthalpic interactions between the polymer brush (PS) and the polymer matrix (PMMA) drives in-plane isotropic phase separation in a fashion similar to binary PS/PMMA homopolymer blend films. The composition-dependent morphologies of this NP-polymer blend film is mapped and the phase separation kinetics with near-critical composition is then compared with the analogous PS/PMMA blend films ( $\approx$  90 nm, upper critical solution temperature estimated as  $T_c \approx 200 \text{ °C}^{18}$ ). A measure of phase stability is confirmed by shallow quench phase separation kinetics at 180 °C and deep quench behavior to 140 °C, as discussed below. The typical spinodal decomposition kinetic regimes for binary polymer blend films, namely, diffusive, hydrodynamic coarsening and late stage 'pinning' regimes, are observed for both NP-polymer blends and polymer-polymer blends. However, the kinetic pathway of the polymer brush-induced phase separation is dominated by the nanoparticle mobility (higher at 180 °C) rather than the thermodynamic driving force (higher at 140 °C), that shows an opposite trend to corresponding binary polymer blends behavior.

To further exert control over the large scale organization of phase-separated AuPS domains, we exploit 'pattern-directed phase separation' in which phase separation symmetry is broken by external perturbations. Previous work has shown that long-range ordered structures were achieved in polymer blends, block copolymer films, and polymer nanocomposites by topographically or chemically patterned substrates<sup>19-21</sup> or interference lithographic exposure,<sup>22</sup> which results in modulated optical and nanomechanical properties.<sup>23,24</sup>

Unlike previous approaches, herein instead of tuning the interfacial interactions with the substrate, the symmetry breaking of co-existing NP-rich and polymer-rich phases is achieved through confinement by a topographically patterned soft overlayer. By this method, long-range ordered submicron-wide strip or cross-hatch lattice (rhombic) patterned AuPS domain structures are autonomously generated with a dense yet randomly well-dispersed nanoparticles distribution inside. This simple physical pattern directed nanoparticle assembly method allows the fabrication of micro- to nano-sized NP domains with well-controlled shape, size and periodicity, enabling many potential applications requiring nanoparticle patterning such as electromagnetic shielding,<sup>25</sup> plastic electronics,<sup>26</sup> nanophotonic devices,<sup>27</sup> and sensors.<sup>28</sup>

#### **Results and Discussion**

We first present a description of thermal annealing induced phase separation morphologies in the AuPS / PMMA blend system, followed by comparative kinetics of phase separation at different temperatures and relative to corresponding homopolymer blends, and finally the topographic pattern directed AuPS arrangements in PMMA matrix.

**Phase separation morphology.** Top-view transmission electron microscopy (TEM) micrograph in Fig. 1 revealed that AuPS nanoparticles were homogeneously distributed within the PMMA matrix in as-cast films. The surface of the blend film was smooth with a root mean

square (rms) roughness,  $R_{rms} \approx 0.4$  nm. This initial random dispersion of NPs resulted from the good dispersion of AuPS in PMMA/toluene polymer solutions before kinetic trapping of nanoparticles during flow-coating. Isotropic phase separation in AuPS/PMMA blend films with AuPS loading (*f*), from 20 % to 80 % (all percentages are given as mass percentages of AuPS nanoparticles relative to the PMMA mass) was induced by 16 *h* vacuum oven annealing at 180 °C, a temperature significantly higher than the glass transition temperatures ( $T_g$ ) of both PS and PMMA ( $T_g PS \approx 90$  °C,  $T_g PMMA \approx 105$  °C). As shown in Fig. 1, depending on the loading fraction of AuPS, the phase separated morphology ranges from discrete AuPS-rich droplet structures (f = 20 %, 40 %) to bicontinuous structures (f = 50 %), to inverted continuous majority phase structures (f = 80 %). Importantly, within each AuPS domain the nanoparticles are not in an aggregated state (see magnified inset image in Fig. 1).



Figure 1. Phase-separated morphology transition of AuPS/ PMMA blend thin films. The left-most image is top-view TEM micrograph for as cast 40% AuPS/PMMA films ( $\approx$  90 nm) with an AFM height image inset. Following adjacent top-view TEM micrographs with AFM phase image insets show classic phase morphology inversion of AuPS/PMMA films with increasing AuPS loading (f = 20 - 80%), upon vacuum oven annealing at 180 °C for 16 h. (Scale bar: 500 nm) The inset TEM micrograph in 20% AuPS image is a zoom-in image for an individual AuPS domain. (Scale bar: 100 nm) Scan size for AFM images is 2 µm.

This composition-dependent morphology transition of AuPS/PMMA blend films is normally found in immiscible binary polymer blends, as confirmed by phase separation morphology of analogous PS/PMMA blend films (Supporting Information, Fig. S1). However, some of the AuPS nanoparticles are clearly segregated to the interface between the coexisting

phases and thus the AuPS-rich domains are 'decorated' by these excess nanoparticles exhibiting compatibilization behavior. This effect is especially prevalent at high nanoparticle loading (f = 80 %). A similar effect has been observed in lamellar block copolymer island growth with addition of nanoparticles which reside at the boundary of islands.<sup>29</sup>

To reveal the mechanism for the observed similarity between the NP-polymer system and binary homopolymer blends phase separation, a suitable PS homopolymer counterpart of AuPS nanoparticle needs to be determined so that the NP-polymer phase separation can be compared with the 'parent blend'. Towards this consideration, we might alternatively imagine the grafted PS ligands to be akin to an individual grafted chain, a star molecule, or a linear PS molecule with mass equal to the sum of all polymer ligands grafted on one particle. Existing theory offers little guidance on this question, but judging from the quasi-equilibrium composition-dependent morphology map (Fig. 1), the critical composition ( $f_c$ ) of AuPS/PMMA blend is  $\approx 50$  %, which roughly matches the calculated  $f_c \approx 60$  % for PS/PMMA blends where the molecular mass of PS is the same as one individual ligand ( $M_{n,PS}$  = 11 kg/mol). Thus, the phase separation of a "parent" PS homopolymer ( $M_{n,PS} = 11.5$  kg/mol) blended with the same PMMA matrix was investigated as comparison to AuPS/PMMA blends. Since the AuPS nanoparticles are densely grafted ( $\sigma^{-1/2}$  <  $R_{g, PS (11.5k)}$ ,  $\sigma$  is grafting density) with a 5.6 nm thick PS brush layer, the van der Waals interactions between gold cores should be effectively screened<sup>7</sup> and the NP-polymer interaction is mainly dictated by the PS ligand/PMMA melt interactions.<sup>30</sup> We then conclude that the phase separation of these AuPS/PMMA blend films is driven by the unfavorable enthalpic interactions between the grafted PS ligands and the free PMMA chains ( $\chi_{PS-PMMA} \approx 0.037$ , 180 °C<sup>18</sup>). This enthalpic driving force for phase separation is further confirmed by the uniform distribution of AuPS in PS matrices with a wide range of molecular masses upon thermal annealing.



Figure 2. Surface topography and internal structure comparison for annealed AuPS/ PMMA and PS/PMMA films. a and c are AFM 3D height images of 40% AuPS/ PMMA and 40% PS/PMMA "parent" blend films annealed at 180 °C for 6 *h* before (left) and after (right) selective removal with cyclohexane, respectively. **b** and **d** are corresponding height profiles for the marked lines (I, II, III, IV) in AFM images. Note the AFM scan size difference for AuPS/PMMA (5  $\mu$ m) and PS/PMMA (90  $\mu$ m) blend films.

Next, we focus on the comparative surface topologies of the NP-polymer and the parent homopolymer blend films upon annealing at 180 °C. Atomic force microscopy (AFM) combined with selective dissolution of AuPS or PS domains with cyclohexane revealed the quasi-3D phase-separated morphology. Figure 2a shows the smooth surface topography [ $R_{rms} \approx (1.1 \pm 0.1)$ nm] of 40% AuPS/PMMA phase-separated films after thermal annealing at 180 °C for 6 *h*. Both PS and PMMA were present at the polymer-air surface and there was a slight increase of PS area fraction from 75.4% to 78.6% upon annealing at 180 °C for 16 *h*, as shown by x-ray photoelectron spectroscopy (XPS) measurements. No wetting layer was observed since the surface energies of PS and PMMA are similar and the interfacial tension between PS and PMMA ( $\gamma_{PS/PMMA} = 1.26 \text{ mJ/m}^2$ , 180 °C) <sup>31</sup> is greater than surface energy difference. The spreading

parameter is negative and thus neither polymer can spread on the other.<sup>32,33</sup> After selective removal of the AuPS phase with cyclohexane, almost all the nanoparticles were removed (Supporting Information, Fig. S2) and holes were identified with average depth of  $(62.4 \pm 0.4)$  nm as shown in Figure 2a, 2b. This implies that the AuPS domains are not patches floating at the film surface; rather they are embedded as phase-separated "troughs" into the 90 nm blend film. The volume fraction of the AuPS troughs compared to the total film volume, estimated from AFM images, is  $\approx 22$  %, in close match to the volume fraction of  $\approx 23$  % of the AuPS in the blend film by composition (40 %). Thus, all of the AuPS is in the trough domains, consistent with TEM observations.

In contrast, upon annealing the parent homopolymer blend (40% PS/PMMA) films for 6 h, we observed the formation of large micron-sized PS phase droplets suspended on a PMMA wetting layer on the substrate (Figure 2c, 2d), with a significantly higher roughness,  $R_{rms} \approx (75.7 \pm 3.6)$  nm. Selective dissolution of PS domains revealed PMMA rims surrounding the surface segregated PS droplet domains, which is consistent with previous literature.<sup>32</sup> Comparison of the trough-like topography of AuPS domains and the large PS droplet phase implies a lower interfacial tension between AuPS and PMMA than that in PS/PMMA blend. This interfacial tension difference can be attributed to the sterically hindered interaction of PMMA chains with the inner layer of the grafted PS brush, analogous to star-linear polymer blends.<sup>34,35</sup> When comparing the interactions between PMMA and end-grafted PS chains versus linear PS chains, different from star-linear polymer blends, it seems more appropriate to consider a single grafted PS chain instead of all the grafted chains on one particle together. As mentioned earlier, the composition-dependent phase separation behavior of AuPS nanoparticles is more analogous to the linear PS counterpart with the same molecular weight as one grafted chain. Detailed

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comparison between grafted nanoparticles and star polymer with the same number of arms will be demonstrated in further studies.

**Phase separation kinetics**. The phase separation evolution of 40 % AuPS/ PMMA (near critical composition) blend films is investigated at different temperatures and compared with the behavior of parent blends (40% PS/ PMMA). In particular, the molecular mass of the linear PS homopolymer is the same as the molecular mass of one individual PS ligand. Figure 3a displays the representative TEM snapshots of 40% AuPS/PMMA films vacuum oven annealed at a relatively lower temperature of 140 °C for different time intervals between 8 *min* and 16 *h*.



**Figure 3.** Phase separation morphology evolution and temperature quench effects for AuPS/ PMMA and PS/ PMMA blend films. Top-view TEM micrographs for 40% AuPS/ PMMA (a) and 40% PS/ PMMA (b) films annealed at 140 °C, and 40% AuPS/ PMMA films annealed at 180 °C for selected time intervals as indicated. Scale bars: 200 nm (a, b) and 500 nm (c).

The uniform as-cast AuPS nanoparticle distribution was disrupted within 8 min annealing,

via spinodal decomposition and the phase separation scale increased with increasing annealing

time. After 1 h annealing, the darker bicontinuous AuPS domain structures broke up into discrete

domains, as expected of the minority phase, and further increase in annealing time (up to 16 *h*) induced moderate growth of these AuPS domains. Similarly, the phase separation of 40% PS/ PMMA films was also initiated by quickly forming a spinodal pattern with a phase separation scale comparable to the AuPS/ PMMA blend films (Fig. 3b). However, the PS phase became the continuous phase upon 2 *h* of annealing, as opposed to the discrete AuPS domains in NP-polymer blend films. This seeming anomaly in morphology is readily explained by the fact that the PMMA substrate wetting layer in PS/PMMA blend films was ~ 60nm (measured in PS extracted films), compared to a thinner ~30nm wetting layer in the AuPS/PMMA blend films. The thick PMMA wetting layer shifts the PMMA from being the majority phase to effectively becoming the minority phase in the PS/PMMA blend films.

The phase separation evolution of the NP-polymer and homopolymer blend films are quantified by the logarithmic relationship between the characteristic wavenumber  $q^*(t)$  and annealing time (Fig. 4a). The values of  $q^*(t)$  at different annealing time *t* are determined from the 2D fast Fourier transform (FFT) radial power spectra at the maximum intensity of the corresponding TEM micrographs. As displayed in Fig. 4a, for 40 % AuPS/PMMA films,  $q^*(t)$  exhibits three distinct regimes depending on annealing time, characterized with a power law,  $q^*(t) \sim t^n$ , where n equals  $0.3 \pm 0.02$ ,  $-1.0 \pm 0.01$  and 0. The overall domain coarsening process is consistent with our previous study on binary polymer blend film phase separation.<sup>36</sup> Specifically, the first regime  $[q^*(t) \sim t^{-1/3}]$  corresponds to the intermediate stage of blends phase separation. It is characterized by coarsening of bicontinuous structures *via* diffusive domain growth according to Lifschitz-Slyozov (LS) law.<sup>37</sup> A similar pattern of spinodal growth kinetics have been also observed for PS-C<sub>60</sub> nanocomposite films.<sup>38,39</sup> The second regime  $[q^*(t) \sim t^{-1}]$  is the late stage coarsening regime, where the phase separated domains coarsen due to the

hydrodynamic instability.<sup>40</sup> The last timeindependent regime  $[q^*(t) \sim t^0]$  is the late stage 'pinning' regime of thin film phase separation that we have studied in previous work.<sup>36</sup> The 'pinning' stage occurred after 2 *h* of annealing when the average AuPS domain radius ( $\approx$  94 nm) was comparable to the film thickness ( $\approx$  90 nm) and the domain growth was constrained by the dimensionality of thin film. In comparison, we only observed late stage hydrodynamic coarsening regime followed by the 'pinning' stage for the same annealing time range in

the PS/PMMA blends.

The kinetics of NP-polymer and parent polymer blends phase separation at a higher temperature of 180 °C (shallow quench) display quite contrasting features compared to that at 140 °C (deep quench). As shown in Fig.



Figure 4. Power-law correlations between the dominant correlation length  $q^*(t)$  and annealing time t for 40% AuPS/ PMMA and 40% PS/ PMMA blend films annealed at 140 °C (a) and 180 °C (b), respectively. Error estimate of the exponents is obtained from a least-squares fit and does not reflect systematic errors.

3c, the spinodal decomposition initiated NP-polymer phase separation rapidly evolved into discrete AuPS domains within 5 *min*, and experienced slight domain growth afterwards. Although reminiscent of the phase separation morphology development at 140 °C (Fig. 3a), the phase separation scale is significantly higher at 180 °C for the same annealing time, especially at

the very beginning. This is attributed to the alteration of the component viscosity and interfacial tension with temperature.<sup>41</sup> Moreover, the coarsening exponent *n*, as displayed in the log-log plot of  $q^*(t)$  in Fig. 4b, shows that only the late stage hydrodynamic regime  $[q^*(t) \sim t^{-1}]$  and a gradual transition to final pinning regime were captured in this annealing time range (15 *s* to 16 *h*). The absence of the intermediate diffusive regime at 180 °C implies a faster kinetic transition at higher annealing temperature for NP-polymer blends. In the same annealing time range at 180 °C, the 40 % PS/PMMA homopolymer blend films exhibited a transition from diffusive, to hydrodynamic and then to 'pinning' regime. During the hydrodynamic regime, the characteristic length scale of phase separation increased dramatically, and the homopolymer blend film morphology ended up with large micro-sized PS phase droplets suspended on the PMMA wetting layer<sup>32</sup>, resulting in a highly undulated film surface (Fig. 2c). At 140 °C, the large PS droplets morphology was not observed in the time period under study due to the higher viscosity at lower temperature.<sup>42</sup>

Comparison of the kinetic regimes for PS/PMMA blend films at different annealing temperatures (Fig. 4a and 4b) reveals that deeper quench (140 °C) with respect to the phase separation boundary induces a faster transition from intermediate diffusive to late stage hydrodynamic regime because of the enhanced thermodynamic driving force. Interestingly, the kinetic regime shift trend is the opposite for NP-polymer blends, where shallow quench (180 °C) leads to an earlier transition to hydrodynamic regime, indicating that the phase separation kinetics was determined by the diffusivity of the components (higher at 180 °C) instead of thermodynamic driving force controlled by quench depth.

**Pattern directed phase separation.** Now that we have established the nature of the phase separation behavior of these NP-polymer blend films, we exert further control over the

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phase separation morphology by a topographically patterned elastomer template, for potential technologically relevant applications such as nanowires. The essential idea is to exploit the inherent sensitivity of phase separation to external symmetry-breaking perturbations. The topographic perturbation introduced patterned is bv а channel cross-linked poly(dimethylsiloxane) (PDMS) overlayer made from commercial DVD template (pitch  $\lambda = 750$ nm, amplitude A = 120 nm). As shown schematically in Fig. 5a, after thermal annealing confined with the strip patterned PDMS overlayer, the nanoparticle arrangement was modified according to the topographic pattern.



Figure 5. Channel pattern directed phase separation in AuPS/PMMA blend films. a, Schematics for channel patterned elastomer confined thermal annealing and the resultant segregation of AuPS domains to one side of the mesas. b, AFM 2D height images for imprinted 40% AuPS/PMMA blend film and the residual film after selective removal of AuPS domains. Scale bar: 500 nm. c and d, Top-view TEM micrographs for AuPS/PMMA blend films (f = 20 % and 40 %) annealed at 180 °C for 10 *min* under channel patterned confinement. Scale bars: 500 nm (c) and 200 nm (d). e, Film thickness variation orthogonal to channel direction (plotted from Fig. 5b) and the corresponding AuPS nanoparticle number distribution ( $N_{AuPS}$ ) (counted from Fig. 5d).

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During this thermal annealing process with soft confinement, the NP-polymer blend films ( $\approx$  90 nm) filled into the channel patterns within seconds *via* a capillary force induced mold filling process, <sup>43-45</sup> generating patterned blend films with alternating trenches ( $\approx$  30 nm) and mesas ( $\approx$  150 nm), as shown in the AFM height image in Fig. 5b. The height difference and lateral dimension of the imprinted 40 % AuPS/PMMA blend films closely coincide with the patterned elastomer mold dimensions (Fig. 5e), indicating a high-fidelity of pattern transfer.

Interestingly, and the most important result of this paper, top-view TEM images (Fig. 5c, d) show that nearly all the AuPS nanoparticles are exclusively located in the high (less confining) mesa regions of the patterned blend films after this simple imprinting process. This exclusive partitioning of AuPS in the high mesa regions is further revealed by selective removal of AuPS domains with cyclohexane (Fig. 5b and 5e). This process shows that quite unusually, the AuPS domains are segregated towards one side (right) in the imprinted mesas. While the one-sided segregation behavior is intriguing, based on the AuPS volume fraction, complete filling of the mesas is not expected. We also note that there is usually a dominant scale of phase separation, so the single-sided segregation rather than a random sided distribution is consistent with equidistant lateral spacing arising from a phase separation scale. The reason behind the exact side selection is potentially related to the curvature difference of these DVD strip patterns, and this phenomenon may be explored in further studies.

The temporal aspects of partitioning of nanoparticles aspect is further quantified in Fig. 5d, illustrating how the pattern effectively guided all the AuPS domains into unidirectional long strips along the channel direction at one side of the mesas of the imprinted films. The width of these AuPS strips was tunable by simply varying the nanoparticle loading f under the same channel patterned confinement. As f increased from 20 % to 40 %, the domain width increased

from  $(102 \pm 6)$  nm to  $(187 \pm 9)$  nm. The number distribution of AuPS nanoparticles ( $N_{AuPS}$ ) in the orthogonal direction to channel pattern is plotted in Fig. 5e along with the height profile,

showing the concurrent film thickness variation and nanoparticle sequestration. Similar to chemical pattern directed phase separation, the periodicity of the domain structures is dictated bv the dimension,<sup>46</sup> pattern but the composition match requirement for pattern replication is alleviated since the pattern pitch is not necessarily comparable to the phase separation scale.

The synergy of NPpolymer phase separation and pattern directed self-organization during thermal annealing is revealed by investigation of phase separation kinetics confined by the channel



Figure 6. Kinetics of channel pattern directed nanoparticle assembly. a, Top-view TEM micrographs for 40% AuPS/PMMA blend films annealed under channel patterned confinement at 140 °C for different time periods as indicated. Scale bars: 200 nm (5 *min* to 6 *h*) and 500 nm (8 *h*). b, Dependence of AuPS nanoparticle distribution ( $N_{AuPS}$ ) on annealing time across the channel direction (counted from Fig. 6a) and the corresponding imprinted film thickness profile (grey dashed line).

patterned elastomer. As shown in Fig. 6a, the 1D topographic strip mold pattern was transferred

into the blend films within 5 *min* of annealing at 140 °C and isotropic phase separation was initiated by spinodal decomposition with a characteristic scale  $D \approx 60$  nm. Further annealing (30 *min*) induced domain coarsening and interdomain spacing increase ( $D \approx 330$  nm). Up to this point, the phase separation was not influenced by the channel pattern confinement and an isotropic spinodal pattern spread all over the blend films.

As the annealing time increased to 2 h ( $D \approx 540$  nm), the channel pattern began to interfere with the isotropic phase separated structures, wherein the nanoparticles migrated towards one side of the mesas while retaining continuous structures. The connectivity of AuPS domains gradually broke up at the trenches and formed discrete domain structures in the channel direction (3 h annealing). At 6 h of annealing, viscous fluctuations of the nanoparticle domain strips were suppressed, forming unidirectional AuPS strip domains with a well-defined width. Figure 6b clearly illustrates the progressive preferential segregation of nanoparticles to one edge of the mesa regions with increasing annealing time, which minimizes the unfavorable interaction between PS and PMMA ( $\gamma_{PS/PMMA} = 1.26 \text{ mJ/m}^2$  at 180 °C) by reducing the interfacial area.<sup>31</sup>. Meanwhile, the preferential segregation of AuPS domains to one side (i.e. right side) of the patterned mesas maintains a constant wavelength of inter-strip spacing. The phase-separated PS/ PMMA blend films can also be directed into strip domains sequestered at one side of the mesas in a similar fashion. (Supporting Information, Fig. S7) We also note that these nanoparticle strip domains are not thermally stable and eventually they broke up into 'bamboo-like' structures inside the imprinted mesas upon 8 h of annealing (Fig. 6a), which is ascribed to capillary instability associated with minimization of interfacial contact area between AuPS domains and PMMA matrix.<sup>47,48</sup>



Figure 7. Cross-hatch lattice pattern directed phase separation in AuPS/PMMA blend films. a, schematics for dual imprinting of partially cured elastomer overlayer to generate 2D crosshatch lattice pattern and the following confined thermal annealing of the blend films. b, AFM 3D height images for lattice pattern imprinted 30% AuPS/ PMMA films (left) and the residual film after removal of AuPS domains (right). The corresponding height variations of the marked lines are shown below the AFM images. c, Top-view TEM micrograph for 30% AuPS/PMMA films annealed at 180 °C for 10 *min* under lattice patterned confinement. Scale bar: 1  $\mu$ m. The magnified inset shows well-dispersed nanoparticles in one AuPS domain. The upper right corner inset is 2D FFT image (24  $\mu$ m<sup>-1</sup>×24  $\mu$ m<sup>-1</sup>).

To precisely further manipulate the shape, size and location of AuPS domains, a 2D topographically patterned elastomer overlayer was applied during the thermal annealing process. As shown in Fig. 7a, a 2D cross-hatch lattice patterned elastomer template was generated by imprinting a partially cured channel patterned elastomer layer on another orthogonally placed, fully cured channel pattern, and this lattice patterned elastomer overlayer served to organize the nanoparticle domains in the following thermal annealing process. The topography of replicated blend films is displayed in 3D AFM images in Fig. 7b, where the total amplitude is  $A \approx 120$  nm (height difference from plateau to intermediate step  $\approx 60$  nm) and pitch is  $\lambda \approx 750$  nm. The

internal distribution of AuPS nanoparticles after annealing at 180 °C for 10 *min* is illustrated in Fig. 7c. The phase-separated AuPS domains were beautifully organized into equal-sized domains at each 2D mesa (cross-hatch intersection plateau) with densely dispersed nanoparticles inside. The sequestration of AuPS domains at the cross-hatch intersections was confirmed by its selective removal with cyclohexane (Fig. 7b). The height variations across the lattice pattern before and after AuPS domain removal are compared by AFM line profiles (Fig. 7b) and the volume of AuPS domains was estimated as  $\approx 32$  % with respect to the volume of the residual film (PMMA phase). The phase separation scale is in commensurate with the 2D pattern periodicity as in the case of 1D channel pattern directed phase separation, but the 2D organization of nanoparticle domains is nevertheless thermally stable.

## Conclusions

In summary, we investigated a novel polymer ligand-induced phase separation behavior of AuPS nanoparticles in an immiscible PMMA thin film matrix. The composition-dependent phase separation morphology transition of the AuPS/PMMA blend is demonstrated and the influence of the annealing temperature on phase separation kinetics for this NP-polymer blend was compared to the equivalent parent PS/PMMA blend thin films. In contrast to classic thermodynamic driving force (i.e. quench depth) controlled phase separation kinetics in homopolymer blends, we show that the mobility of nanoparticles (i.e. the proximity of annealing temperature to  $T_g$ ) determines the morphology evolution kinetics in AuPS/PMMA blends. Importantly, the phase-separated AuPS domains with random nanoparticle dispersion can be readily driven to self-assemble into highly ordered submicron-scale 1D strips and 2D lattice patterns with different topographically patterned elastomer overlayer confinement. Our novel results provide a simple yet powerful strategy to localize non-crystalline domains of

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nanoparticles into precisely defined 'imprinted' regions at high packing density with tunable dimensions. The method should be useful for imparting functional colligative nanoparticle properties involving emerging technologies such as photonic waveguides and electromagnetic shielding as it is also roll-to-roll compatible for industrial production scale-up technology.

## Methods

Poly(methyl methacrylate) (PMMA,  $M_{n,PMMA} = 3.1$  kg/mol, polydispersity=1.09) and polystyrene (PS,  $M_{n,PS} = 11.5$  kg/mol, polydispersity = 1.25) were purchased from Polymer Source Inc. and used as obtained.<sup>49</sup> The thiol-polystyrene (PS-SH) grafted gold nanoparticles (AuPS) were synthesized by phase transfer reduction of [AuCl<sup>4</sup>] in the presence of thiol ligands.<sup>50</sup> The average radius of gold core  $R_0 = (1.21 \pm 0.42)$  nm. PS grafting density is  $\sigma = 0.7$ chains/ nm<sup>2</sup>. The thickness of the PS brush ( $M_{n,PS} = 11.5 \text{ kg} / \text{ mol}$ ) is  $R_n = (5.6 \pm 1.6) \text{ nm}$ , calculated from nearest interparticle distance from a monolayer particle film. Upon vacuum oven annealing at 180 °C for 16 h, AuPS nanoparticles experienced subtle size increase to  $R_0 = (1.35 \pm$ 0.48) nm due to thermally instability of the thiol-Au bond.<sup>13,51</sup> PMMA solutions (3 % by mass in toluene) were mixed with appropriate amount of AuPS nanoparticles (mass ratio of AuPS to PMMA is f = 20 % to 80 %) or PS homopolymer (mass ratio of PS to PMMA is 40 %). The mixed solutions were flow coated into thin films with thickness of  $\approx 90$  nm on ultraviolet–ozonecleaned silicon substrates. The film thicknesses were determined by interferometer (F-20 UV Thin Film Analyzer, Filmetrics, Inc.), where the standard uncertainty of film thickness is  $\pm 1$  nm. Blend films of AuPS/PMMA and PS/PMMA were vacuum oven annealed at 55 °C for 6 h to remove residual solvent before annealing at 180 °C or 140 °C for different time periods to induce phase separation. Phase separated AuPS domains (in AuPS/PMMA films) and PS domains (in

PS/PMMA films) were selectively removed by immersing into cyclohexane for 30 *min* at room temperature.

Topographically patterned cross-linked poly(dimethyl siloxane) (PDMS) elastomer templates (thickness  $\approx 0.5$  mm, elastomer: curing agent = 20:1) were made by curing PDMS on a commercial digital video disc (DVD, pitch  $\lambda = 750$  nm, amplitude A = 120 nm). Single imprinting generated a channel pattern, and orthogonal dual imprinting resulted in a cross-hatch lattice pattern. The patterned PDMS overlayer served as top confinement during the following thermal annealing. After annealing, the PDMS overlayer was removed. Films were characterized with a JEOL JEM-1230 transmission electron microscope (TEM) at 200 kV. Specimens for TEM were prepared by pre-coating a thin layer ( $\approx 10$  nm) of aqueous poly(4-styrenesulfonic acid) (PSS; Sigma–Aldrich) solution on to the substrates and vacuum oven annealed at 140  $^{\circ}$ C for 12 h. coating and annealing the blend films, and then floating the films by immersing into distilled water followed by transferring to copper grids. Surface topography was imaged using a Dimension Icon atomic force microscope (AFM) (Bruker Nano) in tapping mode. X-ray Photoelectron Spectroscopy (XPS) was performed on a Kratos AXIS Ultra DLD spectrometer with a monochromated Al  $K_{\alpha}$  source operating at 1486.6 eV and 140 W. The base pressure the sample analysis chamber was nominally  $2.0 \times 10^{-9}$  Pa. Atomic composition was determined from survey scans over a binding energy range of (0 to 1200) eV, a pass energy of 160 eV, and a step size of 0.5 eV. Peak fitting was performed on high resolution scans of the C 1s region collected using pass energy of 20 eV and a step size of 0.1 eV. All data analysis was performed using the CassaXPS software package.

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**Supporting Information.** TEM micrographs for pure AuPS nanoparticle films and 40% AuPS/PMMA films annealed at 180 °C for 6 *h* after selective removal; AFM height images for 40% AuPS/PMMA and 40% PS/PMMA blend films annealed at 180 °C and 140 °C for different time periods and the corresponding film morphology after selective removal; large-area TEM micrographs for channel pattern induced phase separation in 40% AuPS/PMMA films at different time intervals and same effect on 40% PS/PMMA blend films.

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