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# Nanoscale Phase Separation in Mixed Poly(*tert*-butyl acrylate)/Polystyrene Brushes on Silica Nanoparticles under Equilibrium Melt Conditions

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Mixed homopolymer brushes, composed of two chemically distinct polymer chains randomly or alternately immobilized by one end via a covalent bond on a solid surface with high grafting densities, represent a new class of stimuli-responsive materials.[1] It has been a long-standing fundamental issue in polymer science whether symmetric mixed homopolymer brushes on a flat substrate microphase separate laterally or vertically under equilibrium melt conditions. Theoretically, Marko and Witten predicted a lateral phase separation, forming a "rippled" state,[1a] for symmetric mixed brushes on a flat substrate. The transition is expected to occur at a critical molecular weight 2.27 times that for the same homopolymers in a simple blend at its demixing threshold, and the spatial period of the pattern is predicted to be on the order of polymer chain root-mean-square end-to-end distance. However, it is unknown what pattern (random, stripe, or checkerboard) would form on a flat substrate and how the curvature would affect the pattern if the substrate is curved.[1c,g]

In this communication, we report, for the first time, on the study of phase behavior of well-defined mixed poly(*tert*-butyl acrylate) (P*t*BA)/polystyrene (PS) brushes on silica nanoparticles under equilibrium melt conditions. The advantage of using silica nanoparticles rather than silicon wafers lies in the fact that conventional morphology characterization techniques, such as transmission electron microscopy (TEM), can be easily employed, and potentially, the effect of substrate curvature on microphase separation of mixed brushes could be investigated if the size of nanoparticles varies. Two mixed brush samples with different molecular weights were annealed in vacuum above their glass transition temperatures ($T_g$) and were studied by differential scanning calorimetry (DSC) and TEM.

Mixed P*t*BA/PS brushes were synthesized by sequential atom transfer radical polymerization of *tert*-butyl acrylate and nitroxide-mediated radical polymerization of styrene from an asymmetric, difunctional initiator-terminated self-assembled monolayer (Y-SAM) on silica nanoparticles with a diameter of 180 nm.[2] Y-SAM was designed to ensure that the two initiators are alternately distributed in the monolayer so that well-mixed homopolymer brushes can be grown on the surface.[3] Corresponding free initiators were added into the polymerization mixtures to control the surface-initiated polymerizations.[2,3] We confirmed that the molecular weights and polydispersities of the grafted polymers were essentially identical to those of the free polymers formed from free initiators in the solutions.[2] In this study, two samples prepared from the same batch of Y-SAM-coated silica nanoparticles but with different molecular weights were used. The characterization data are summarized in Table 1. The grafting densities of the two polymers were calculated on the basis of thermogravimetric analysis data and the size of bare particles measured from electron microscopy images.[2] For both samples, P*t*BA and PS have similar grafting densities (Table 1), and the average distance between grafting sites was 1.1−1.2 nm. From electron microscopy images, the thicknesses of polymer brushes were ~20 and ~10 nm for samples **I** and **II**, respectively. Thus, the tethered polymers were in the brush regime.

***Table 1.*** Characterization Data for Samples **I** and **II** Composed of Mixed Poly(*tert*-butyl acrylate)/Polystyrene Brushes with Different Molecular Weights on Silica Nanoparticles

| No. | $M_n$, PDI, and DP of P*t*BA[a] | $\sigma_{PtBA}$[b] | $M_n$, PDI, and DP of PS[a] | $\sigma_{PS}$[b] | brush thickness[c] |
|---|---|---|---|---|---|
| **I** | 24200, 1.09, 187 | 2.5 | 23000, 1.10, 221 | 2.7 | ~20 nm |
| **II** | 10400, 1.15, 87 | 3.1 | 11900, 1.19, 114 | 2.9 | ~10 nm |

[a] $M_n$ = number average molecular weight (g/mol), determined by gel permeation chromatography (GPC) analysis relative to PS standards; PDI = polydispersity index; DP = degree of polymerization. The DPs of P*t*BA were calculated by use of monomer conversion and the monomer-to-initiator ratio. The DPs of PS were calculated from the molecular weights measured by GPC. [b] $\sigma$: grafting density of polymer (nm$^2$/polymer chain). [c] Brush thicknesses were measured from electron microscopy images.

Samples **I** and **II** were annealed in vacuum at 150 °C (3 h for sample **I** and 24 h for sample **II**), higher than both $T_g$ values of P*t*BA (34 °C) and PS (100 °C), to achieve thermodynamic equilibrium. For comparison, the corresponding free polymers that were formed from the free initiators in the solutions and the P*t*BA brush-grafted nanoparticles, which were used to prepare mixed brushes, were also annealed at 150 °C. The samples were then used for DSC and TEM studies. For sample **I**, two glass transitions, located at 44 and 90 °C, were observed in the DSC curve (Figure 1A). These two transitions corresponded to the glass transitions of P*t*BA and PS, respectively, suggesting that the two grafted polymers phase separated into microdomains that consisted of nearly pure polymers. Since one end of the polymer chain was tethered to the surface, the phase separation was confined in the brush layer. The $T_g$ of P*t*BA in the mixed P*t*BA/PS brushes was the same as that (44 °C) of P*t*BA homopolymer brushes on silica particles used to prepare the mixed brushes. Note that the $T_g$ of the grafted P*t*BA chains ($M_n$ = 24 200 g/mol) was 10 °C higher than that (34 °C) of the free polymer with the same molecular weight, which is believed to be the result of surface tethering effect. Savin et al. also observed an increase in the $T_g$ for the homopolymer brushes on silica nanoparticles compared to the free polymers.[4] In contrast, sample **II** exhibited only one very broad glass transition with a middle point at 83 °C, implying that the two grafted polymers in this sample did not strongly phase separate. The $T_g$ of P*t*BA brushes with a $M_n$ of 10 400 g/mol was 40 °C, and the free polystyrene with a $M_n$ of 11 900 g/mol exhibited a glass transition at 99 °C. Note that the changes in the heat capacity (proportional to the changes in the heat flow) during glass transitions for all polymer brushes on nanoparticles are appreciably smaller than those for free homopolymers, suggesting restricted mobility of the tethered polymers.

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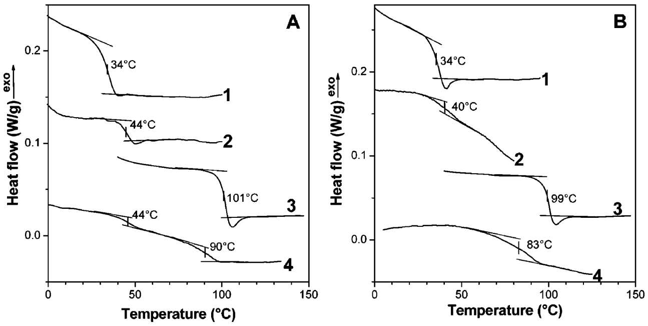

*Figure 1.* Differential scanning calorimetry analysis of (A1) free P*t*BA ($M_n = 24\,200$ g/mol), (A2) P*t*BA brush-grafted nanoparticles ($M_n = 24\,200$ g/mol), (A3) free PS ($M_n = 23\,000$ g/mol), (A4) mixed brushes on silica nanoparticles composed of P*t*BA with a $M_n$ of 24 200 g/mol and PS with a $M_n$ of 23 000 g/mol, (B1) free P*t*BA ($M_n = 10\,400$ g/mol), (B2) P*t*BA brush-grafted particles ($M_n = 10\,400$ g/mol), (B3) free PS ($M_n = 11\,900$ g/mol), and (B4) mixed brushes on nanoparticles composed of P*t*BA with a $M_n$ of 10 400 g/mol and PS with a $M_n$ of 11 900 g/mol. The DSC data for polymer brushes have been normalized on the basis of the polymer weight percentages determined by thermogravimetric analysis.

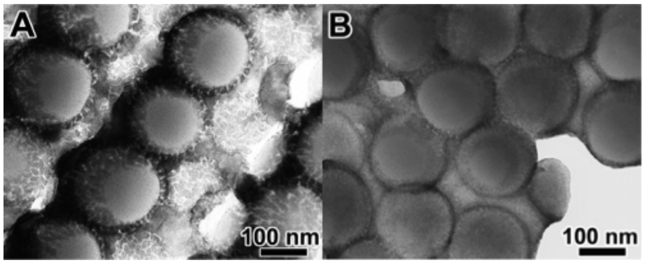

*Figure 2.* Transmission electron microscopy micrographs of thin sections of (A) sample **I** and (B) sample **II** after staining with $RuO_4$ for 30 min. The random worm-like pattern formed from lateral phase separation on the surface of silica nanoparticles in sample **I** can be seen in the lower right part of the image in A.

The thermally annealed samples **I** and **II** were embedded in standard epoxy and microtomed at room temperature using a diamond knife. The thin sections (~50 nm) were stained with $RuO_4$ vapor for 30 min to enhance the contrast. Figure 2 shows the typical TEM micrographs of thin sections of mixed P*t*BA/PS brushes.[5] For sample **I**, the microphase separation of the two grafted polymers in the brush layer with a thickness of ~20 nm can be clearly seen. Without $RuO_4$ staining, the nanoscale structure in the brush layer cannot be observed.[5] The dark and white areas corresponded to PS and P*t*BA microdomains, respectively, as $RuO_4$ was found to stain PS but not P*t*BA homopolymer brushes under the same staining conditions.[5] Clearly, mixed P*t*BA/PS brushes underwent a lateral phase separation under equilibrium melt conditions, and the feature size is around 10 nm, which is on the same order of polymer chain root-mean-square end-to-end distance, consistent with the theoretical prediction,[1a−c] although the brushes are on curved substrates. The pattern formed from the lateral phase separation is random and worm-like, resembling the early stage spinodal decomposition of polymer blends but at a much smaller scale. This is in drastic contrast to ordered molecular segregation (0.5 nm) of thiol molecules on gold nanoparticles.[6]

Although lateral phase separation was clearly seen in sample **I**, the molecular details on the mechanism of microphase separation in mixed brushes are still lacking. First, there must exist a transition zone between the silica surface and the microphase separated mixed brush layer.[1a,b] However, this thin layer was not clear in the TEM images. Further experiments are underway to visualize this transition zone and determine its thickness. Second, a closer examination revealed that in some micrographs there was a thin dark layer (~1 nm) at the outermost layer of the microphase separated brushes (see the arrow in Figure S2 in Supporting Information). This might suggest that, under melt conditions, a very thin PS layer was exposed directly to the air to minimize the surface free energy penalty due to a better affinity of PS to the air. Similar surface organization with PS chains at the outermost layer was also found in PS-*b*-PMMA thin films.[7]

For sample **II**, which was prepared from the same Y-SAM-functionalized silica nanoparticles as for sample **I**, no clear phase separation can be seen in the brush layer from the TEM micrograph, consistent with the DSC result that there was only one broad glass transition (curve B4 in Figure 1). A careful inspection of this micrograph indicated some density fluctuation in the mixed brushes, resembling the density fluctuation-induced disordered phase in block copolymers.[8] To determine at what molecular weighs the two grafted polymers in the mixed brushes begin phase separation, further study is desired and underway.

In summary, using DSC and TEM, we have observed the lateral phase separation in mixed brushes composed of P*t*BA ($M_n$ = 24 200) and PS ($M_n$ = 23 000 g/mol) in melt on curved substrates. The phase separation resulted in a random worm-like pattern with a feature size of ~10 nm. Whether this phase separation can be directed to form regular nanostructures is under investigation.

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**Supporting Information Available:** Experimental Part; TEM micrographs of thin sections of sample **I** with and without $RuO_4$ staining, and thin sections of PS-brush and P*t*BA-brush grafted silica nanoparticles stained with $RuO_4$. This material is available free of charge via the Internet at http://pubs.acs.org.

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(5) TEM micrographs of thin sections of sample **I** stained with $RuO_4$, a thin section of sample **I** without $RuO_4$ staining, a thin section of PS brush-grafted silica nanoparticles stained with $RuO_4$, and a thin section of P*t*BA brush-grafted silica nanoparticles after staining with $RuO_4$ for 30 min can be found in the Supporting Information.
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