

Interfacial Segregation of Hyper-branched Polystyrene in Mixtures of Linear Component

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To study an effect of polymer architecture on surface segregation in polymer mixtures, concentration profile in films composed of hyper-branched polystyrene (HBPS) and deuterated linear polystyrene was examined along the direction normal to the surface by dynamic secondary ion mass spectroscopy. HBPS with two different end groups such as hydrogen and dithiocarbamate (HBPS-H and HBPS-DC) were used. While HBPS-H was preferentially segregated at both surface and substrate interface, HBPS-DC was partitioned only to the substrate interface. These results can be explained in terms of conformational entropic penalty and chain end localization at the surface.

Key words: hyper-branched polystyrenes, surface and interfacial segregation, chain ends

1. INTRODUCTION

Binary polymer mixtures, which are prepared by blending two different polymers, have been extensively used in a wide variety of technological applications because their physical properties and/or functions are sometimes better than the ones predicted simply on the basis of each component.¹ Invoking that thin and ultrathin films of polymer mixtures will be used in industry with the advent of cutting-edge applications based on nano-technology, systematical understanding of aggregation states and physical properties in the surface and interfacial regions of polymer mixtures, which are sometimes quite different from the bulk ones, is of pivotal importance as the first benchmark.

Surface energy of components is generally one of responsible factors for surface segregation in polymer mixtures.²⁻¹⁰ In short, when polymers A and B with lower and higher surface energies, respectively, are mixed, the surface will be covered with the polymer A to minimize the free energy of the system. In addition, chain length is also one of responsible factors for surface segregation; a shorter chain component is partitioned to

the surface.¹¹⁻¹⁶ This has been explained in terms of conformation entropy and/or chain end segregation at the surface. Since surface chains are compressed along the direction normal to the surface,^{17,18} they are supposed to have less conformational entropy than bulk Gaussian chains. The entropic penalty at the surface increases with increasing chain dimension, namely, molecular weight. Thus, it is thermodynamically favorable that shorter chains are segregated at the surface. Besides, chain end groups with surface energy smaller than that of the main chain part are localized at the surface.¹⁹⁻²³ Thus, chains connected to end groups are led out to the surface. The number density of chain ends is larger in shorter chains than longer ones, resulting in a clear chain end effect for shorter chains.

A class of hyper-branched polymer (HBP) would exhibit an intriguing feature as a surface modifier based on its unique architecture.²⁴⁻²⁹ This is because HBP possesses a large number of end groups in one molecule compared to a linear component with a given molecular weight. Besides, the chain dimension of HBP is generally smaller than that of the corresponding linear

component. Therefore, the purpose of this study is to examine to what extent HBP is segregated at the surface in the mixture of the corresponding linear component, if any, so that knowledge of surface segregation in polymer mixtures is enlarged. And, the segregation of HBP at the substrate interface is also discussed.

2. EXPERIMENTAL

Hyper-branched polystyrene (HBPS-H) and the one with dithiocarbamate end groups (HBPS-DC) were synthesized.³⁰⁻³³ Fig. 1 shows the schematic representation of HBPS. Since they have a different kind of chain ends, the chain end effect on surface and interfacial segregation can be clearly seen. As a linear component, monodisperse deuterated polystyrene (dPS), purchased from Polymer Source Inc., was used. Deuterium labeling was necessary to confer a contrast between HBPS and linear component during the following mass spectrometry. Number-average molecular weights (M_n) of HBPS-H, HBPS-DC and dPS were 7.1k, 4.9k and 115k, respectively. Their polydispersity indices were 4.2, 3.9 and 1.04. Also, the densities of HBPS-H, HBPS-DC and dPS were 1.05, 1.17 and 1.13 g/cm³, respectively.

Blends of HBPS and dPS were prepared by mixing each toluene solution. HBPS of 5 weight % was fed to the blend, and this ratio was fixed through all samples employed. Blend films with the thickness of about 200 nm were spin-coated from toluene solutions onto silicon (Si) wafers with a native oxide layer. These films were annealed for 24 h at 423 K, being well above the bulk glass transition temperatures.

Composition profile in the (HBPS/dPS) blend films was examined by dynamic secondary ion mass spectrometry (DSIMS) (SIMS 4000, Atomika Analysetechnik GmbH). To gain access to a stable sputtering during the measurement, the buffer dPS layer with the thickness of approximately 150 nm was laminated onto the (HBPS/dPS) blend film by a floating technique. The incident beam of oxygen ions with 4 keV and ca. 35 nA was focused onto a 300 $\mu\text{m} \times 300 \mu\text{m}$ area of the specimen surface. The incident angle was 45°. A 20 nm-thick gold layer was sputter-coated on the buffer layer surface to avoid a charging of the specimen during the measurement.

3. RESULTS AND DISCUSSION

Fig. 2 shows typical DSIMS profiles of H⁻, D⁻ and C⁻ ions for a (HBPS-H/dPS) blend film. H⁻ and D⁻ ions were originated from the HBPS and the matrix dPS, respectively. At first, the outmost gold layer was etched.

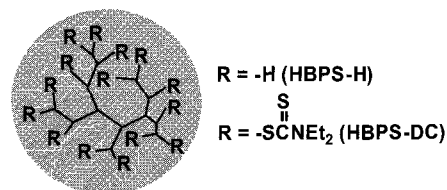


Fig. 1. Schematic representation of HBPS.

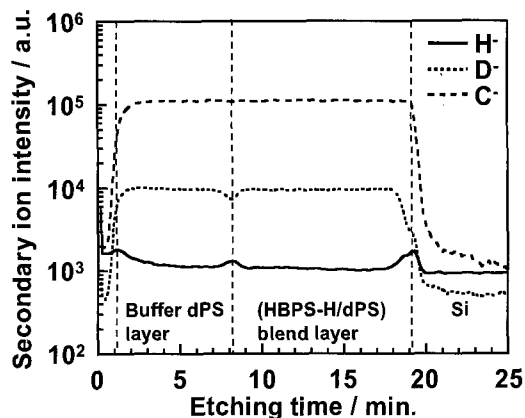


Fig. 2. DSIMS profiles of hydrogen (H⁻), deuterium (D⁻), and carbon (C⁻) ions for a (HBPS-H/dPS) blend film.

Hence, secondary ions from the polymers were not clearly detected. After a minute, the C⁻ intensity started to increase, and then, remained an almost constant through the sample. This indicates that the steady-state etching proceeded during the measurement. Since the etching rate for the measurement, which was pre-examined using a film with a well-defined thickness, was known, the border between the buffer dPS layer and the blend film can be identified. This border, of course, corresponds to the surface of the blend film. The identification of the substrate interface was much easier than the surface's case because the secondary ion intensity of Si⁻ can be used as a marker of the Si wafer. The H⁻ and D⁻ intensities at the surface and substrate interface were, respectively, higher and lower than those in the interior region in the blend. This makes it clear that HBPS-H was preferentially segregated at the air and substrate interfaces.

The abscissa of etching time in Fig. 2 can be simply converted to the depth from the surface. The vertical axis in Fig. 2 can be also converted to HBPS weight fraction (ϕ_{HBPS}) on the basis of secondary ion intensity via the following equation.³⁴

$$\phi_{\text{HBPS}} = f_{\text{HBPS}}^{\text{wt}} z_0 I_{\text{HBPS}^-}(z) / \int_0^{z_0} I_{\text{HBPS}^-}(z) dz$$

where $f_{\text{HBPS}}^{\text{wt}}$, z_0 and $I_{\text{HBPS}^-}(z)$ are weight fraction of

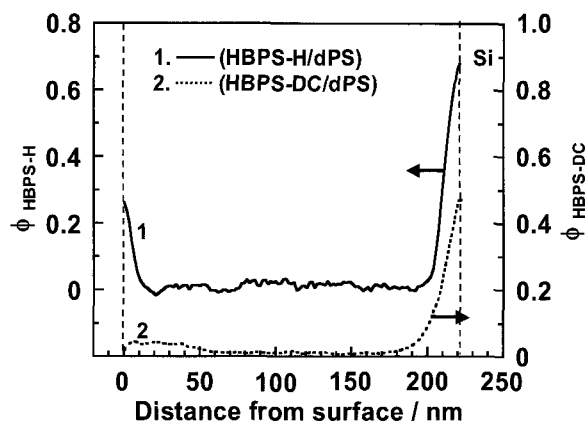


Fig. 3. Concentration profiles of HBPS-H and HBPS-DC in blend films.

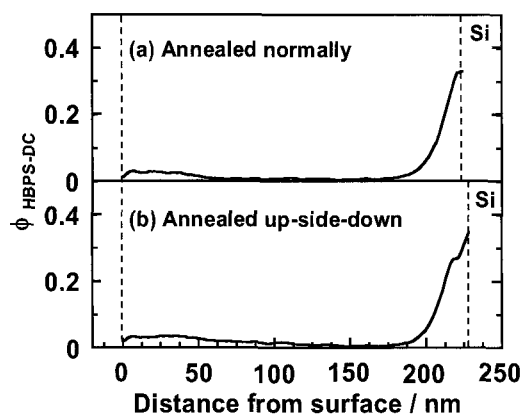


Fig. 4. Concentration profiles of (HBPS-DC/dPS) blend films; (a) normally annealed (b) annealed up-side-down.

HBPS, film thickness and secondary ion intensity originated from HBPS at depth of z , respectively.

Fig. 3 shows concentration profiles of HBPS-H and HBPS-DC in the blend film. Although the bulk fraction of HBPS-H in the blend was fixed to be 5 wt %, the surface and interfacial fractions were apparently 30 and 70 at %, respectively. It is worthy to note that HBPS-H was not almost existed in the interior region of the film. Since the profile was convoluted by the instrumental broadening function, the real compositions at the surface and interface must be larger than those values. The surface segregation of HBPS-H can be easily explained in terms of conformational entropy and/or chain end effect, as stated in introduction section. These factors may be responsible for the interfacial segregation as well. In order to discuss to what extent the both effects are important, the same experiment must be done using hyper-branched polystyrene with a different kind of end groups such as HBPS-DC. In the

case of the (HBPS-DC/dPS) blend, hyper-branched polymer was again segregated at the substrate interface. However, the extent became less in comparison with the (HBPS-H/dPS) blend. Besides, at the surface, a clear segregation of HBPS-DC was not observed, as shown by the bottom curve in Fig. 3.

End groups of HBPS-DC are relatively hydrophilic, resulting in no surface segregation of end groups. This eventually led to no segregation of HBPS-DC at the surface. Thus, it is conceivable that the chain end effect is definitely responsible for the surface segregation of hyper-branched polymers in addition to the conformational entropic penalty at the surface. At first, it was expected that dithiocarbamate end groups were thermodynamically favorable to the substrate interface and thus the interfacial segregation of hyper-branched component was more prominent than that in the (HBPS-H/dPS) blend film. However, that was not the case. If we assume that the chain dimension of HBPS-DC is not as small as that of HBPS-H due to the presence of dithiocarbamate groups, the entropy-driven segregation of HBPS-DC would be less effective than that of HBPS-H. This explanation is also consistent with an experimental result that HBPS-DC was not segregated at the surface. However, for the moment, it is too early to conclude which factor, conformational entropic penalty or chain end segregation, is more dominant for the surface and interfacial segregation of hyper-branched polymers. We will report more conclusive discussion using monodisperse hyper-branched samples in the near future.

Finally, an effect of density on the surface segregation in polymer mixtures is discussed because the density of HBPS-DC is much larger than that of dPS. If the density effect acted against thermodynamic factors and dominated the system, HBPS-DC cannot be existed at the surface, as experimentally observed in Fig. 3. Thus, a (HBPS-DC/dPS) blend film was put in a vacuum oven up-side-down and then annealed under the same condition as usual. The bottom curve in Fig. 4 shows depth profile of the (HBPS-DC/dPS) blend film so annealed. For comparison, depth profile of the (HBPS-DC/dPS) film normally annealed is also shown at the upper part of Fig. 4. A major discrepancy was not observed in the two profiles. Thus, it can be envisaged that the density effect on the segregation phenomena in polymer mixtures should be trivial, if any.

4. CONCLUSIONS

Using hyper-branched polymers, effects of conformational entropic penalty and chain end

localization on surface and interfacial segregations in polymer mixtures were discussed. Experimental results clearly showed that both factors are definitely important. However, more experiments are necessary to conclude which factor dominates the phenomena.

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