

Surface Segregation of Well-defined *N*-Substituted Hyperbranched Polyamides in Linear Polymer Matrix

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Surface segregation of well-defined *N*-substituted hyperbranched polyamides (HBPA) with various side chain lengths in linear polystyrene matrix was studied. To what extent HBPA was segregated at the surface was dependent on the side chain length, which regulated intermolecular interactions among HBPA molecules via steric hindrance.

Simple and cost effective technologies for creating functional polymer surfaces have been desired. To this end, numerous methods have been proposed.¹ These conventional methods, however, generally need multistep processes. On the other hand, the surface treatment we here propose is based on a single process. Functional molecules are mixed into a polymer, in which the surface characteristics should be altered, leading to the preferential segregation at the surface.

When two polymers with a similar degree of polymerization are mixed, the lower surface energy component is enriched at the surface.² The molecular weight disparity between the components also causes the surface segregation of the smaller component.³ The latter can be explained in terms of less conformational or translational entropic penalty for the shorter chain at the surface in addition to the surface localization of chain end groups.

Hyperbranched polymers (HBP) have a tremendous potential as highly functionalized materials due to the large number of chain ends.⁴ If chain ends have a smaller surface energy than the repeating unit, they act as buoys.⁵ Thus, when HBP is mixed into a linear polymer, HBP is partitioned to the surface. In addition, the chain dimension of HBP is smaller than that of a linear polymer with comparable molecular weight. This also leads to the surface segregation of HBP in a matrix polymer. Therefore, it seems that HBP is a promising candidate as a surface modifier.⁶

So far, various types of HBP have been synthesized. A general disadvantage of HBP is that the primary structure is not clear, so that complications arise in understanding its fundamental properties. Thus, in this letter, we use well-defined *N*-substituted hyperbranched polyamides (HBPA) with different lengths of side chains⁷ to study the segregation behavior at the surface. In the case of *N*-substituted polyamides, the different side chain length alters molecular interaction with one another. Thus, the effect of molecular interaction on the surface segregation can be discussed.

HBPA with various lengths of *N*-alkyl side chain were synthesized by a method previously reported.⁷ Figure 1 shows the chemical structure of HBPA. The number-average molecular weight (M_n) and polydispersity index (PDI) of HBPA were evaluated by gel permeation chromatography (GPC) with a multiangle laser light scattering (MALLS) detector.⁸ The M_n so

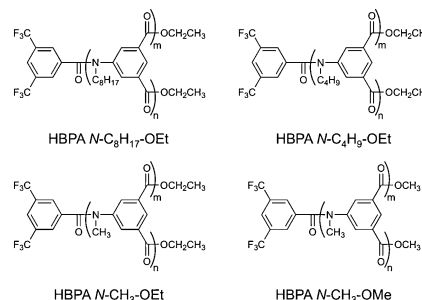


Figure 1. Chemical structure of HBPA with various side chain lengths.

obtained for HBPA *N*-C₈H₁₇-OEt, HBPA *N*-C₄H₉-OEt, HBPA *N*-CH₃-OEt, and HBPA *N*-CH₃-OMe were 9.4×10^3 , 11.2×10^3 , 23.4×10^3 , and 24.7×10^3 , respectively.⁹ The PDI of HBPA was approximately 1.1 for all. As a linear component, monodisperse PS with the M_n of 290×10^3 was used. Blend solutions were prepared by mixing tetrahydrofuran solutions. The fraction of HBPA in the blend was fixed to be 5% in weight. Blend films with a thickness of about 200 nm were spin-coated onto silicon wafers with a native oxide layer. These films were annealed for 24 h at 393 K. The surface composition of the blend films was examined by X-ray photoelectron spectroscopy (XPS, PHI 5800 ESCA system, physical Electronics Co., Ltd.) with AlK α source operated at 14 kV and 200 mA. The analytical depth of XPS is given by $3\lambda \sin \theta$, where λ and θ are the inelastic mean-free path of the photoelectron in the solids and the emission angle, respectively. The inelastic mean-free path of C_{1s} photoelectrons was taken as 2.9 nm, calculated by Ashley's equation.¹⁰ The depth profile of HBPA composition in the vicinity of the surface was discussed on the basis of angular-dependent measurement.

Figure 2 shows the XPS survey scan spectra for the blends acquired at θ of 45°. Since fluorine and nitrogen existed only in HBPA, the detection of F_{1s} and N_{1s} peaks by XPS means that HBPA is present at the surface to a depth down to 6.2 nm. The intensity of fluorine and nitrogen peaks decreased with decreasing alkyl side chain length.

To study the composition profile in the HBPA/PS blend films, angle-resolved measurement was made for the two blends where HBPA was clearly present in the surface region. Figure 3a shows the integral intensity ratio of F_{1s} to C_{1s} ($I_{F_{1s}}/I_{C_{1s}}$) for the HBPA *N*-C₈H₁₇-OEt/PS and *N*-C₄H₉-OEt/PS blend films. The $I_{F_{1s}}/I_{C_{1s}}$ value was much larger than in the bulk, calculated on the basis of the blend composition, and also increased with decreasing $\sin \theta$. These results make it clear that HBPA *N*-C₈H₁₇-OEt and *N*-C₄H₉-OEt were preferentially segregated at

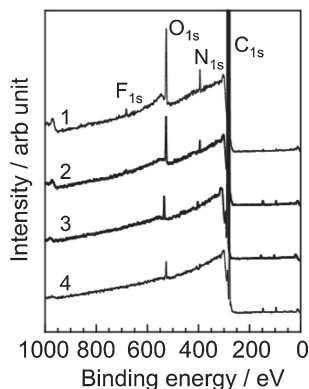


Figure 2. XPS wide-scan spectra for PS blends mixed with HBPA (1) *N*-C₈H₁₇-OEt, (2) *N*-C₄H₉-OEt, (3) *N*-CH₃-OEt, (4) *N*-CH₃-OMe.

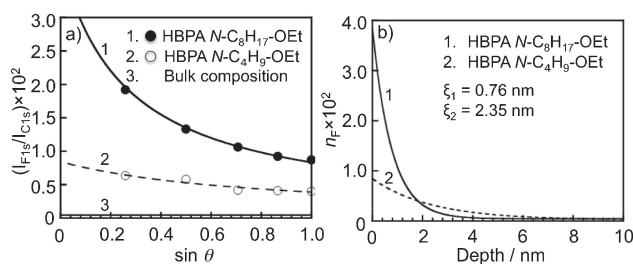


Figure 3. (a) $\sin\theta$ dependence of XPS intensity ratio of F_{1s} to C_{1s} for HBPA *N*-C₈H₁₇-OEt/PS and HBPA *N*-C₄H₉-OEt/PS. (b) Model profile of fluorine to best-fit to the experimental results shown in (a).

the surface. The extent of the segregation was more striking for *N*-C₈H₁₇-OEt than for *N*-C₄H₉-OEt.

To convert the panel (a) to the relation between real depth vs. I_{F1s}/I_{C1s} , the mean-field-approximation is adopted to express the composition profile of HBPA as follows,¹¹

$$n_F(z) = n_{F,\infty} + (n_{F,s} - n_{F,\infty}) \exp(-z/\xi) \quad (1)$$

where z and ξ are the distance from the outermost surface and the decay length showing how the surface composition reaches the bulk value, respectively, and $n_{F,s}$ and $n_{F,\infty}$ are the surface and bulk composition of fluorine. The curves 1 and 2 in Figure 3a, calculated from the profiles in the panel (b), are the best-fit to the experimental results. The ξ value is related to the chain dimension of components involved.¹¹ Thus, Figure 3b implies that *N*-C₄H₉-OEt possesses a larger molecular weight than *N*-C₈H₁₇-OEt. Although this is not necessarily in agreement with the sample characterization, the following explanation should be plausible.

Here, it should be noteworthy to discuss why the segregation ability of HBPA is a function of alkyl side chain length. So far, many researchers have reported that linear polyamides possess a strong intermolecular interaction among main chains. One of the typical and intriguing results is that the crystallinity of well-controlled *N*-substituted linear polyamide is strongly affected by the alkyl side chain length.¹² In the case of a shorter side chain, crystalline structure is formed. On the other hand, no crystalline structure is formed for polyamide with longer chains because of steric hindrance via inhibition of the attractive interaction among main chains. If this notion can be simply

applied to our current HBPA samples, the intermolecular interaction of HBPA should be in the order of HBPA *N*-C₈H₁₇-OEt, HBPA *N*-C₄H₉-OEt, and HBPA *N*-CH₃-OEt from a weaker side. Then, HBPA with a shorter alkyl side chain might form aggregates, leading to an increase in apparent molecular weight. This is entropically unfavorable to be segregated at the surface, as stated in the introduction. This hypothesis could well explain the trend appeared in Figures 2 and 3.

We finally come to the effect of chain end groups on the surface segregation. This is crucial for HBPA because an ample number of chain end groups are present per a molecule. The effect can be seen in the difference between HBPA *N*-CH₃-OEt and HBPA *N*-CH₃-OMe shown in spectra (3) and (4) of Figure 2, respectively. While the peak of fluorine could not be clearly seen for both cases due to the low concentration, the nitrogen peak could be seen for HBPA *N*-CH₃-OEt/PS blend film. To quantitatively discuss the molecular interaction of chain end groups, glass-transition temperature (T_g) was measured by differential scanning calorimetry.¹³ The T_g value of HBPA *N*-CH₃-OEt and HBPA *N*-CH₃-OMe was 395 and 423 K, respectively. This implies that the molecular interaction of HBPA *N*-CH₃-OMe is stronger than that of *N*-CH₃-OEt, and leads to a speculation that HBPA *N*-CH₃-OEt is better segregated at the surface. This is actually what can be seen in Figure 2.

In conclusion, we have demonstrated that the molecular interaction of a component regulates the extent of the segregation. This knowledge can be used to design a promising surface modifier.

We thank Mr. Hironori Atarashi, Kyushu Univ. for his helpful comments and fruitful discussions. This research was partly supported by Grant-in-Aids for Young Scientists A (No. 21685013) and for the Global COE Program, "Science for Future Molecular Systems" from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

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- 8 The M_n value of hyperbranched polymer estimated by GPC is generally lower than the real M_n value and therefore was calculated by division of the M_w value from MALLS by the M_w/M_n ratio from GPC. Here, M_w is the weight-average molecular weight.
- 9 The degree of branching values, estimated by ¹H NMR spectrum, of HBPA *N*-C₈H₁₇-OEt, HBPA *N*-C₄H₉-OEt, HBPA *N*-CH₃-OEt, and HBPA *N*-CH₃-OMe were 0.33, 0.34, 0.53, and 0.51, respectively.
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