766 *Macromolecules* **2007,** *40,* 766−769

Critical Brush Density for the Transition between Carpet-Only and Carpet/Brush Double-Layered Structures. 2. Hydrophilic Chain Length Dependence

Hideki Matsuoka,* Yasuyuki Furuya, Ploysai Kaewsaiha, Emiko Mouri,[†] and Kozo Matsumoto

Department of Polymer Chemistry, Kyoto University,
Kyoto 615-8510, Japan

Received August 7, 2006
Revised Manuscript Received November 12, 2006

Introduction

Ionic amphiphilic diblock copolymers form monolayers on the water surface when the hydrophobic segment length is long enough.[1] The monolayer consists of a hydrophobic layer on the water and a hydrophilic layer just beneath the water surface. Although the hydrophilic layer is expected to be a polyelectrolyte brush structure,[2] it is not a simple layer but has a carpet + brush double-layered structure when the hydrophilic segment is long enough and the brush density is high enough.[3−9] If the degree of polymerization of the hydrophilic segment is less than 50 or the brush density is very low or both, only the carpet layer is formed without a brush layer.[8] The carpet layer, which has also been confirmed by other researchers,[10,11] is the hydrophilic layer with a very high density (close to the bulk value) and is thought to be formed to avoid the contact between the hydrophobic layer and water subphase, in other words, to reduce the interfacial free energy. By using X-ray reflectivity (XR) and neutron reflectivity (NR)[7] techniques, which are unique techniques for in situ study of the monolayer on the water surface, we have been clarifying the nanostructure and its change by the surface pressure, π, chain length, and salt concentrations for weakly ionic amphiphilic diblock copolymer[3−9] and strongly ionic amphiphilic diblock copolymer.[12] The weak acid polymers were found to have a dependency on salt concentration different from that of strong acid polymers was found. In addition, for strongly ionic amphiphilic diblock copolymers, existence of the "critical salt concentration" has been found where salt concentration dependence changes.[12]

To clarify the condition and requirement for the carpet + brush double-layered structure, we investigated the nanostructure and its change for weakly ionic diblock copolymer, (diethylsilacyclobutane)$_m$-*b*-(methacrylic acid)$_n$, monolayer as a function of brush density in our previous study.[13] The brush density was controlled not only by changing the area/molecule (A) value by the Langmuir−Blodgett (LB) trough but also by addition of the hydrophobic homopolymer to keep the hydrophobic layer thickness constant. As a result, we have found the critical brush density was 0.48 nm^{-2} for the transition from carpet-only to a carpet + brush double-layered structure for m:n = 34:50 polymer independent of the hydrophobic layer thickness.

In this study, we evaluated the critical brush density for polymers with different hydrophilic segment lengths. By applying the same procedure, we have observed the transition and its critical density for all the polymers used. The critical brush density thus obtained was found to be dependent on the hydrophilic chain length. This observation could be interpreted by the constant thickness of the carpet layer.

Table 1. Characteristics of Diblock Copolymers, Poly(diethysilacyclobutane)-*b*-poly(methacrylic acid)

m:n[a]	M_n[a]	M_w/M_n[b]
34:50	8900	1.16
27:67	9500	1.06
33:93	12 500	1.05
29:155	16 800	1.11
(Et2SB)$_{29}$-*b*-COOH	4000	1.07

[a] Determined by ^{1}H NMR of parent polymer in CD_2Cl_2. [b] Determined by GPC of parent polymer with polystyrene standards. Solvent: chloroform for block copolymer; THF for homopolymer.

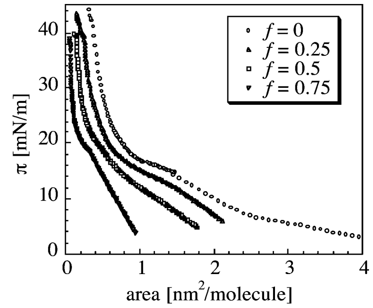

Figure 1. π−A isotherms for $(Et_2SB)_{27}$-*b*-$(MAA)_{67}$ with four different f conditions.

Experimental Section

Materials and Monolayer Preparation. The diblock copolymers, (diethylsilacyclobutane)$_m$-*b*-(methacrylic acid)$_n$ (PEt$_2$SB-*b*-PMAA) with m:n = 27:67, 33:93, and 29:155 were newly synthesized in addition to the polymer used in our previous study (m:n = 34:50) by the procedure reported previously.[14] The homopolymer mixed was also the same as that in our previous study. The polymers used were purified and characterized as reported. The characteristics for each polymer are summarized in Table 1 together with those for the m:n = 34:50 polymer used in our previous study since the data for this polymer would be discussed and analyzed also in this work.

***π*—*A* Isotherm and X-ray Reflectivity Measurements.** The surface pressure (π) vs the area per molecule (A) curves were measured as previously reported.[4−9,13] The brush density was controlled as reported previously, i.e., by changing A and mixing the homopolymer, in the range from 0.098 to 0.82 chain/nm^2. XR profiles were measured by RINT-TTR-MA (Rigaku Corp., Tokyo, Japan), as previously described elsewhere.[15] The fitting procedure, fitting accuracy and data analyses were as reported previously.[13]

Results and Discussion

Figures 1, 2, and 3 show π−A isotherms for the monolayer for three polymers with different m:n as a function of mixing ratio f (the molar ratio of homopolymer mixed in the mixture with block copolymer). As was the case for our previous study on m:n = 34:50 polymer, the isotherm shifted toward smaller A values with increasing f, in other words, with increasing the amount of homopolymer mixed. This is quite understandable since the brush density decreases with increasing f, which results in a decrease of steric hindrance and/or electrostatic repulsion between hydrophilic chains under the water surface.

Figures 4, 5, and 6 show XR profiles for polymer monolayers on the water surface. Each profile corresponds to a different f

---

* To whom correspondence should be addressed. E-mail: matsuoka@star.polym.kyoto-u.ac.jp.

[†] Present address: Department of Applied Chemistry, Kyushu Institute of Technology, Kitakyushu 804-8550, Japan.

10.1021/ma061789m CCC: $37.00

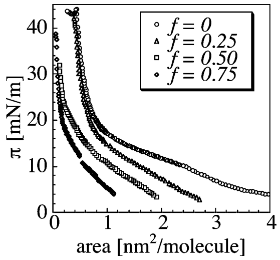

Figure 2. $\pi-A$ isotherms for $(Et_2SB)_{33}$-*b*-$(MAA)_{93}$ with four different *f* conditions.

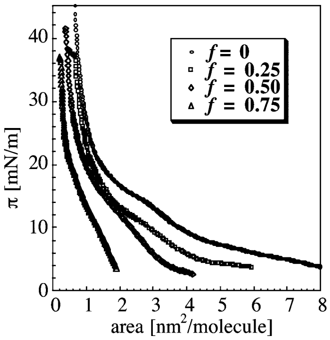

Figure 3. $\pi-A$ isotherms for $(Et_2SB)_{29}$-*b*-$(MAA)_{155}$ with four different *f* conditions.

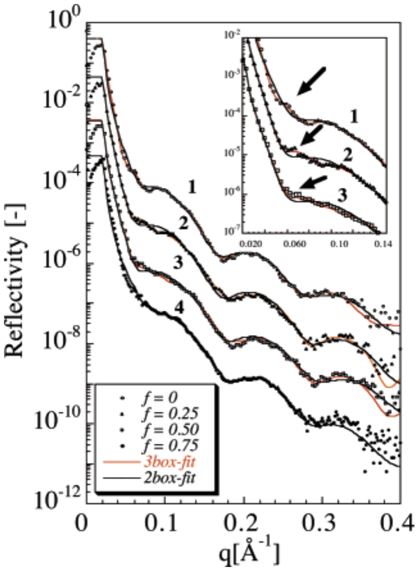

Figure 4. XR profiles for $(Et_2SB)_{27}$-*b*-$(MAA)_{67}$ monolayers on water surface with four different *f* conditions. Black lines show fitting by the two-box mode. Red lines show fitting by the three-box model. The inset is a magnification of small *q* regions to clarify the difference of two-box and three-box model fittings (indicated by n arrow). The hydrophobic layer thickness d_{SB} was kept at about 57 Å.

value, but the thickness of the hydrophobic layer was kept almost constant by tuning the *A* values (and hence the π values). As was observed previously,[4−9,13] very clear Kiessig fringes were observed for all three polymers used in this study. Also, a small fringe at about $q = 0.06$ is observed in this study clearer than in a previous study on the critical brush density.[13] As reported previously, this small fringe is due to the carpet/brush double-layered structure and is very sensitive to structural transition from carpet-only structure to carpet/brush double-layered structure.[6] This small fringe can be reproduced only when we use a three-box model (hydrophobic, carpet, and brush layers) to fit the XR profiles (red lines in the figures). On the other hand, profiles without a small fringe could be satisfactorily fitted by a two-box model (hydrophobic layer and carpet layer) (black lines in the figures). This situation can be more clearly seen in the inset of each figure, which is a magnification of small *q* regions. The structural parameters of the monolayers on the water, such as thickness of each layer were thus estimated.

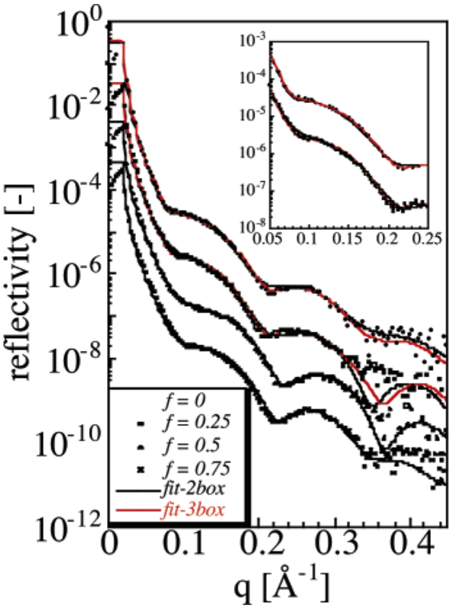

Figure 5. XR profiles for $(Et_2SB)_{33}$-*b*-$(MAA)_{93}$ monolayers on water surface with four different *f* conditions. Black lines are fitting by the two-box mode. Red lines are fitting by the three-box model. The inset is a magnification of small *q* regions to clarify the difference of two-box and three-box model fittings. The hydrophobic layer thickness d_{SB} was kept at about 45 Å.

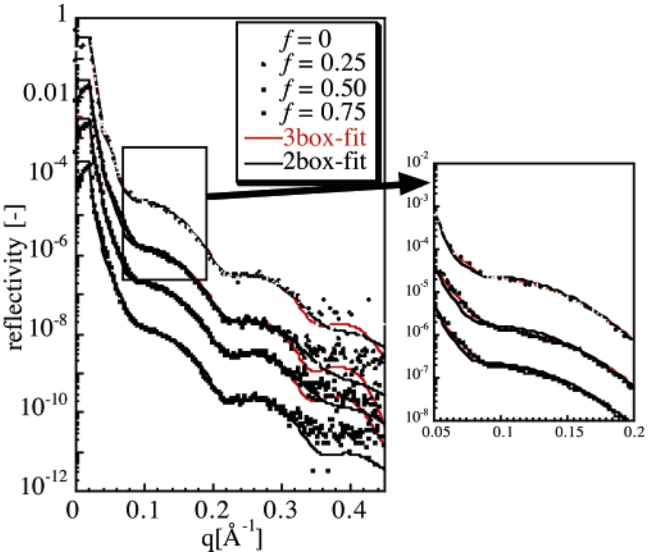

Figure 6. XR profiles for $(Et_2SB)_{29}$-*b*-$(MAA)_{155}$ monolayers on water surface with four different *f* conditions. Black lines are fitting by two-box mode. Red lines are fitting by a three-box model. The inset is a magnification of small *q* regions to clarify the difference between two-box and three-box model fittings. The hydrophobic layer thickness d_{SB} was kept at about 44 Å.

Figures 7, 8, and 9 are histograms showing the thickness of each layer, i.e., hydrophobic, carpet, and brush layers, for three polymers used as a function of brush density with almost constant hydrophobic layer thickness conditions. The height of the upper direction bar represents the thickness of hydrophobic layer. The height of the lower direction bar corresponds to the hydrophilic layer thickness. Its darker part represents the

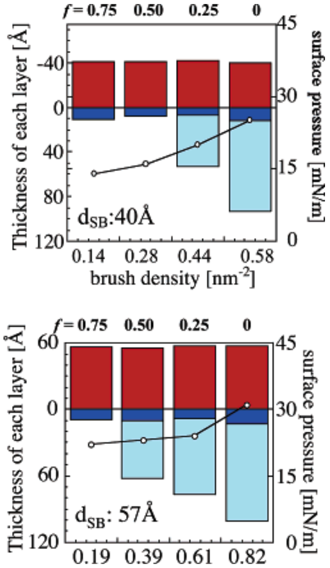

Figure 7. Histogram representation of the thickness of hydrophobic layer (upper bar), carpet layer (darker lower bar), and brush layer (lighter lower bar), when existing, as a function of the brush density determined by in site XR measurement for $(Et_2SB)_{27}$-*b*-$(MAA)_{67}$ monolayers on the water surface at almost a constant hydrophobic layer thickness at 40 and 57 Å. The circles are surface pressure as a function of brush density (right axis).

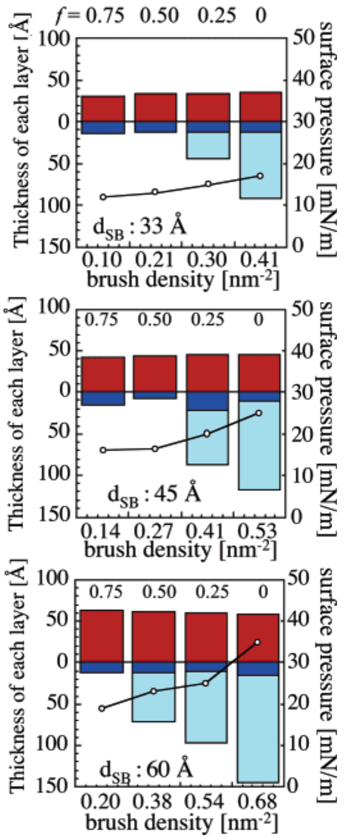

Figure 8. Histogram representation of the thicknesses of hydrophobic layer (upper bar), carpet layer (darker lower bar), and brush layer (lighter lower bar), when existing, as a function of the brush density determined by in site XR measurement for $(Et_2SB)_{33}$-*b*-$(MAA)_{93}$ monolayers on the water surface at almost the constant hydrophobic layer thickness at 33, 45, and 60 Å. The circles are surface pressure as a function of brush density (right axis).

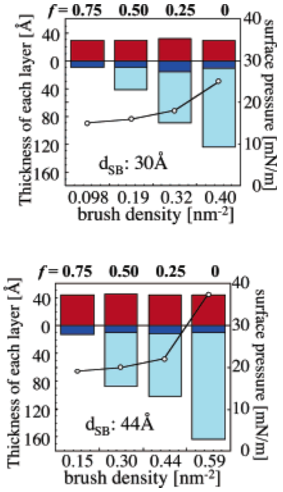

Figure 9. Histogram representation of the thickness of hydrophobic layer (upper bar), carpet layer (darker lower bar), and brush layer (lighter lower bar), when existing, as a function of the brush density determined by in site XR measurement for $(Et_2SB)_{29}$-*b*-$(MAA)_{155}$ monolayers on the water surface at almost a constant hydrophobic layer thickness at 30 and 44 Å. The circles are surface pressure as a function of brush density (right axis).

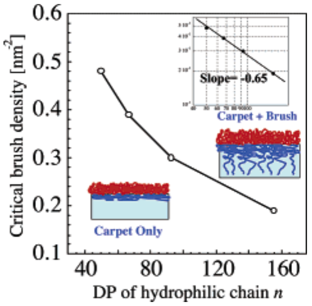

Figure 10. Critical brush density as a function of the degree of polymerization of the hydrophilic chain. The inset is the double-logarithmic plot.

carpet layer thickness and the lighter part the brush layer thickness when existing. As was the case in our previous study, a transition from carpet-only structure to carpet/brush double-layered structure is observed for all the three polymers used. From these results, we evaluated the "critical brush density", at which the transition occurs, to be about 0.39, 0.30, and 0.19 nm^{-2} for m:n = 27:67, 33:93, and 29:155 polymers, respectively. Obviously, the critical brush density depends on the n value.

Figure 10 shows the critical brush density thus determined as a function of the hydrophilic chain length. The value for m:n = 34:50 polymer determined by our previous study is also included. The critical brush density for m:n = 34:50 was 0.48 chain/nm^2, which was so high that only three chains could be inserted between neighboring grafted chains. As clearly seen in Figure 10, the critical brush density decreases with increasing hydrophilic chain length. For m:n = 29:155 polymer, the critical density is as low as 0.19 nm^{-2}, which is still a rather high value. This tendency can be understood if we take the change of the carpet layer thickness into account. As we reported previously,[4−9,13] the thickness of the carpet layer is always kept constant at about 10−20 Å independent of the surface pressure, hydrophilic chain length, and salt concentration. This tendency was also confirmed for the strongly ionic polyelectrolyte brush which has sulfonic acid groups.[12] This trend is also observed in the present study; as clearly seen in Figures 7−9, the thickness of the carpet layer is kept constant at about 10−20 Å independent of the PMAA length, hydrophobic layer thickness, and the brush density, although a slight error for the absolute value is noted.

The tendency observed in Figure 10 can be understood when this constancy of the carpet layer thickness is considered. The constant carpet layer thickness means that the amount of hydrophilic chain for carpet layer formation per unit area is constant. Hence, the longer hydrophilic chain can form a brush layer at a lower brush density than shorter hydrophilic chain.

As we reported previously, the constancy of the carpet layer thickness is significant information for understanding the thickness of "Interface". Since a contact of the hydrophobic layer with water increases the interfacial free energy, the hydrophilic chain forms a dense carpet layer to avoid the contact. The constant thickness of the carpet layer, of about 10−20 Å, means that this thickness is enough to minimize the interfacial free energy. In other words, the hydrophobic layer does not feel the existence of water phase below the carpet layer when the carpet layer thickness is at about 10−20 Å. Since further thickening has no advantage for the system, the hydrophilic chains start to form a brush layer with increasing brush density. With the interpretation above, the tendency of the critical brush density in Figure 10 is quite easily understandable and acceptable. The inset of Figure 10 is the double-logarithmic plot. Quite excellent linearity is observed, with a slope of about −0.65, although the physical meaning of this power low is unclear at this moment. There are some theories on the polyelectrolyte brush,[16] but the existence of a carpet layer is never considered.

Needless to say, the constant carpet layer thickness should depend on the hydrophobicity of the segment, and also the tendency to form a brush layer should depend on the character of the hydrophilic chain. The absolute value of the critical brush density and its dependency on the chain length will be systematically investigated in the future. We have already started a similar transition study on the ionic diblock copolymer monolayer having a strong acid character.[17]

Conclusion

The critical brush densities for the transition between carpet-only and carpet + brush double layer structures were systematically investigated for a weakly ionic amphiphilic diblock copolymer, (diethylsilacyclobutane)$_m$-*b*-(methacrylic acid)$_n$, monolayer on the water by an in situ X-ray reflectivity technique. The critical brush density was found to be dependent on the degree of polymerization of the hydrophilic segment, n, and decreased from 0.48 to 0.19 nm^{-2} with increasing n from 50 to 155. On the other hand, the thickness of carpet layer was observed to be almost constant at 10−20 Å. The dependence of the critical brush density on n could be reasonably understood by taking this constant carpet layer thickness into account. Although there is still no theoretical background for the carpet layer formation, the carpet-only/carpet + brush structural transition certainly exists and it has found to be systematically depending on the chain length. At least in the amphiphilic block copolymer monolayer, the polyelectrolyte brush does not always exist but formed only when the interfaces are suitably stabilized. Further investigation on the universality of the carpet layer thickness and the absolute value of the critical brush density, and also its salt concentration effect, is now underway. The information on this "critical brush density" should prove to be very important to the control of the brush nanostructure and to establish the tailor-made surfaces.

Acknowledgment. This work was supported by a Grant-in-aid for Scientific Research (No. A15205017) from the Ministry of Education, Culture, Sports, Science, and Technology of Japan, to whom our sincere gratitude is due. This work was also supported by the 21st Century COE Program, COE for a United Approach to New Materials Science.

References and Notes

(1) *Block Copolymers in Solution*; Hamley, I. W., Ed.; Wiley: Chichester, England.
(2) *Polymer Brushes*; Advincula, R. C.; Brittain, W. J.; Caster, K. C.; Rühe, J. Eds.; Wiley-VCH: Weinheim, Germany.
(3) For a convenient review, see: Mouri, E.; Matsuoka, H. In *Encyclopedia of Nanoscience and Nanotechnology*; Marcel Dekker: New York, 2004; pp 2519−2529.
(4) Mouri, E.; Wahnes, C.; Matsumoto, K.; Matsuoka, H.; Yamaoka, H. *Langmuir* **2002**, *18*, 3865.
(5) Mouri, E.; Matsumoto, K.; Matsuoka, H. *J. Appl. Crystallogr.* **2003**, *36*, 722.
(6) Mouri, E.; Matsumoto, K.; Matsuoka, H. *J. Polym. Sci., B,* **2003**, *41*, 1921.
(7) Mouri, E.; Matsumoto, K.; Matsuoka, H.; Torikai, N. *Langmuir* **2005**, *21*, 1840.
(8) Mouri, E.; Furuya, Y.; Matsumoto, K.; Matsuoka, H. *Langmuir* **2004**, *20*, 8062.
(9) Mouri, E.; Kaewsaiha, P.; Matsumoto, K.; Matsuoka, H.; Torikai, N. *Langmuir* **2004**, *20*, 10604.
(10) Ahrens, H.; Förster, S.; Helm, C. A. *Phys. Rev. Lett.* **1998**, *81*, 4172.
(11) Yim, H.; Kent, M. S.; Huber, D. L.; Satija, S.; Majewski, J.; Smith, G. S. *Macromolecules* **2003**, *36*, 5244.
(12) Kaewsaiha, P.; Matsumoto, K.; Matsuoka, H. *Langmuir* **2004**, *20*, 6754.
(13) Matsuoka, H.; Furuya, Y.; Kaewsaiha, P.; Mouri, E.; Matsumoto, K. *Langmuir* **2005**, *21*, 6842.
(14) Matsumoto, K; Wahnes, C.; Mouri, E.; Matsuoka, H.; Yamaoka, H. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 86.
(15) Matsuoka, H.; Mouri, E.; Matsumoto, K. *Rigaku J.* **2001**, *18*, 54.
(16) Borisov, O. V.; Zhulina, E. B.; Birshtein, T. M. *Macromolecules* **1994**, *27*, 4795.
(17) (a) Matsuoka, H.; Kaewsaiha, P.; Suetomi, Y.; Matsumoto, K. *Polym. Prep. Jpn*, **2006**, *54*, 3889. (b) Kaewsaiha, P.; Matsumoto, K.; Matsuoka, H. *Langmuir* **2007**, *23*, 20.

MA061789M