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Association of block copolymers with dendritic and perfluorinated side chains in solution and at an interface

Abstract Block copolymers, poly(3,5-bis(3,5-bis(benzyloxy)benzyloxy)benzyl methacrylate-*random*-methacrylic acid)-*block*-poly(2-perfluorooctylethyl acrylate) [P(D₃MA,MAA)-*b*-PFA], which contain benzyloxy dendron and perfluorinated alkyl chains in their side chains, were synthesized. The products were characterized by differential scanning calorimetry and IR absorption spectroscopy, and their degrees of polymerization were determined with gel permeation chromatography, elemental analysis, and UV-vis spectroscopy. It was confirmed from transmission electron microscopic and atomic force microscopic observation that P(D₃MA,MAA)-*b*-PFAs were associated into polydisperse, spherical particles in a chloroform solution. The surface pressure–area isotherms

of Langmuir monolayers at the air–water interface displayed hysteresis, which was remarkable for a P(D₃MA,MAA)-*b*-PFA with a medium substitution fraction of the dendron block. The molecular orientation at the air–water interface estimated from atomic force microscope images of Langmuir–Blodgett films depended on the substitution fraction: Whereas the atomic force microscope image of a Langmuir–Blodgett film of a copolymer with a medium substitution fraction showed a flat surface, that with the high fraction showed a zone texture.

Keywords Block copolymer · Dendron · Perfluorinated alkyl chain · Surface pressure–molecular area isotherm · Atomic force microscopy

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Introduction

Fluorinated polymers are useful materials owing to their low surface energy and thermal stability [1–18]. Especially, block copolymers which have a fluorocarbon side chain in one block and a solvophilic side chain in the other block exhibit great potential owing to their fluorocarbon character and amphiphilicity. Then, the copolymers can form self-assembled, ordered structures at the interface and micellar structures in the solution. Their self-assembling properties can be controlled by the changes of the chemical structure, i.e., the length and the ratio of hydrophobic and hydrophilic segments [19–21].

The fluorinated diblock copolymers poly(methyl methacrylate)-*block*-poly(2-perfluorooctylethyl methacrylate) (PMMA-*b*-PFMA) and poly(methacrylic acid)-*block*-poly(2-perfluorooctylethyl methacrylate) (PMAA-*b*-PFMA) consist of a randomly coiled solvophilic block and a rigid perfluorinated block [22, 23]. PMMA-*b*-PFMA forms small micelles in organic solvents, whereas PMAA-*b*-PFMA in methanol is associated into larger micelles than PMMA-*b*-PFMA and the size of its micelles depends cooperatively on the pH in the aqueous medium.

It is expected that when side chains of the PMAA block in PMAA-*b*-PFMA are replaced by bulky

dendrons, the whole block copolymer should become rigid and have different properties from the original block copolymer. In the present work, we report the characterization of block copolymers with dendritic and perfluorinated side chains, poly(3,5-bis(3,5-bis(benzyloxy)benzyloxy)benzyl methacrylate-*random*-methacrylic acid)-*block*-poly(2-perfluorooctylethyl acrylate) [P(D₃MA,MAA)-*b*-PFA] and their association behavior in solution and at the interface.

Polymers that have dendritic side chains have been reported by some researchers [24–37]. Förster et al. [29] have investigated how dendron side chains stiffen the polymer backbone by means of small-angle neutron scattering. Bo et al. [30] synthesized amphiphilic polymers with dendrons and hydrophobic alkyl chains. With the development of science, multifunctional polymer materials are demanded. Copolymers consisting of a perfluorinated block and a dendron block, which are investigated in the present work will be attractive as novel multifunctional materials. However, such block copolymers have never been reported, as far as we know.

Experimental

Dendron, 3,5-bis(3,5-bis(benzyloxy)benzyloxy)benzyl bromide, was purchased from Tokyo Kasei Kogyo Co. and other chemicals were of commercial grade. Diblock copolymer, poly(methacrylic acid)-*block*-poly(2-perfluorooctylethyl acrylate) (PMAA-*b*-PFA, lot no. M2), was synthesized by eliminating, with concentrated hydrochloric acid, the *t*-butyl methacrylate (*t*-BMA) side chains of poly(*t*-butyl methacrylate)-*block*-poly(2-perfluorooctylethyl acrylate), which was synthesized by radical polymerization from *t*-BMA and 2-perfluorooctylethyl acrylate as monomeric units and polyperoxide as initiator.

Thermal properties were analyzed using differential scanning calorimetry (DSC). First heating was scanned from 30 to 150 °C at an elevation rate of 10 °C min⁻¹, and then the polymers were cooled down to 30 °C at a rate of 5 °C min⁻¹. Subsequently, a second heating, scanned from 30 to 200 °C at a rate of 10 °C min⁻¹, was carried out. Fourier transform IR (FT-IR) absorption spectra were recorded at room temperature (about 25 °C) using a Bio-Rad FTS 575C FT-IR spectrometer. KBr pellets of the compounds were prepared.

The molecular weight was determined using a Shimadzu SCL-10A gel permeation chromatogram (GPC). The eluent for the GPC was tetrahydrofuran (THF), and polystyrene was used as a standard of molecular weight. During the measurement, the temperature was kept at 40 °C. UV-vis spectra of THF solutions of the polymers and a dendron were measured at 25 °C with a Shimadzu UV-2200 spectrometer. Elemental analysis was carried out with an LCO CHN-900 elemental analyzer.

A Hitachi H-800 transmission electron microscope (TEM) was used to take photographs of the cast films on carbon-coated copper TEM grids from a methanol solution (1.0 mg cm⁻³) of M2 and chloroform solutions (1.0 mg cm⁻³) of M2den (Table 1). A Digital Instruments NanoScope III microscope was used to get the atomic force microscope (AFM) images of cast films and Langmuir-Blodgett (LB) films on mica. Microscopic observations were done at room temperature (about 25 °C).

A LB film deposition apparatus (Nippon Laser & Electronics Laboratory) was used to measure surface pressure-surface area (π -*A*) isotherms. A small amount of a chloroform solution (1.0 mg cm⁻³) of the polymer was spread on the water subphase in the trough, and 30 min was allowed for solvent evaporation. Isotherms were measured at a compression rate (barrier speed) of 5 mm min⁻¹ at a subphase temperature of 25 °C. Optical imaging of the monolayer on the water subphase was observed by a Brewster-angle microscope (Nippon Laser & Electronics Laboratory NL-EMM63) placed over a Langmuir film balance.

LB films were prepared at a surface pressure of 20 mN m⁻¹. The Langmuir film was transferred onto a mica substrate for the AFM observation. The Z-type and ZX-type LB films were prepared by one upstroke transfer and additional downstroke transfer to the Z-type film, respectively, at a rate (dipping speed) of 2 mm min⁻¹. After the transfer, the LB films were dried in vacuo for 8 h.

Results and discussion

Synthesis and characterization of block copolymers

PMAA-*b*-PFA (1.0 g for lot no. M2den1 or 0.19 g for lot nos. M2den2 and M2den3), 3,5-bis(3,5-bis(benzyloxy)benzyloxy)benzyl bromide (1.0 g for M2Den1 and M2den2 or 3.0 g for M2Den3) and 1,8-diazabicyclo[5.4.0]undec-7-ene (0.20 g) were dissolved in 10 cm³ dimethyl sulfoxide, and the solution was heated at 50 °C for 5–16 h (Scheme 1). Then the solution was acidified with three drops of hydrochloric acid (12 N), and poured into excess methanol (200 cm³). The resultant

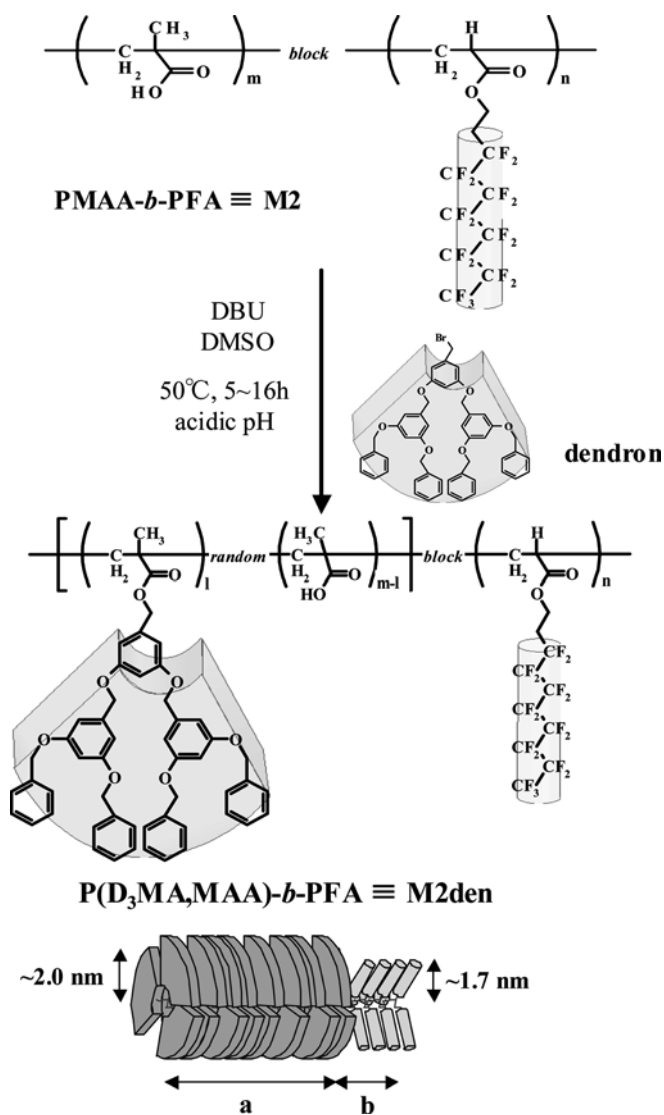
Table 1 Characterization of block copolymers

Lot no.	$M_n/10^{3a}$	M_w/M_n^a	Number of dendrons ^b	C:H ratio ^c	Composition				Molecular length/nm			Collapse pressure/ mN m ⁻¹	Occupied molecular area/nm ² molecule ⁻¹
					<i>l</i>	<i>m-l</i>	<i>n</i>	<i>m+n</i>	<i>a</i>	<i>b</i>	<i>a+b</i>		
M2	25.9	1.29	0	3.39:3.58	0	123	29	152				30–40	
M2 den1	8.3	1.19	2.5	3.99:4.81	3	55	3	61	12.6	0.7	13.3		
M2 den2	25.9	1.70	23.7	6.15:5.47	24	12	11	47	7.8	2.4	10.2	20–25	12 (solid state), 18 (liquid state)
M2 den3	27.1	1.72	28.0	6.16:5.45	28	2	8	38	6.5	1.7	8.2	13–20	17 (solid state)

^aFrom gel permeation chromatography

^bFrom UV-vis spectra

^cFrom elemental analysis



Scheme 1

precipitates were separated from the solution, washed with water (800 cm³), and dried in vacuo. Since the degree of substitution of the PMAA block should depend on the ratio of the 3,5-bis(3,5-bis(benzyloxy)benzyloxy)benzyl bromide dendron to PMMA-*b*-PFA, the products are random copolymers including the PMAA block and the dendron block and must be described as poly(3,5-bis(3,5-bis(benzyloxy)benzyloxy)benzyl methacrylate-*random*-methacrylic acid)-*block*-poly(2-perfluorooctylethyl acrylate) (M2den), where the degrees of polymerization of the PD₃MA, PMAA, and PFA blocks are denoted *l*, *m-l*, and *n*, respectively (Scheme 1).

In the DSC thermogram of the second heating process on the M2den copolymer, the melting temperature, T_m of the perfluorinated block was observed at 67.5 °C (M2den1), 68.5 °C (M2den2), or 67.5 °C (M2den3) as

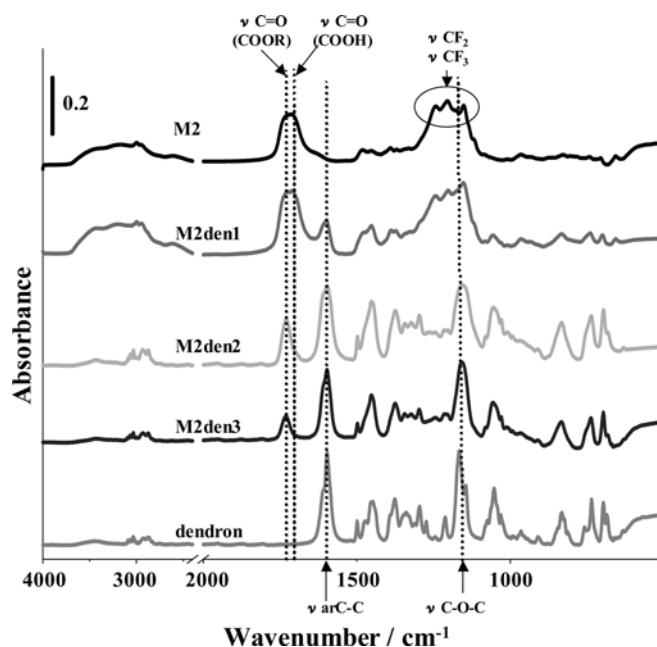


Fig. 1 IR absorption spectra of KBr pellets of block copolymers and dendrons

an endothermic peak. Additionally, the glass-transition temperature, T_g , of the dendron block was observed at 46.2 °C (M2den₂) or 41.8 °C (M2den₃) as the midpoint of the transition. This indicates the replacement of methacrylic acid by the dendron.

The replacement was confirmed even from IR spectra. As seen in Fig. 1, the spectrum of PMAA-*b*-PFA displayed ester C=O and carboxylic acid C=O stretching vibration bands at 1,730 and 1,713 cm⁻¹, respectively. CF₃ asymmetric, CF₂ antisymmetric, and CF₂ symmetric stretching bands appeared at 1,243, 1,204, and 1,152 cm⁻¹, respectively. The bands originating from PMAA-*b*-PFA weakened relatively with the replacement of methacrylic acid by the dendron, and absorption bands characteristic of the dendron strengthened. The bands at 1,596 and 1,156 cm⁻¹ are assigned to the benzene ring C-C and ether C-O-C antisymmetric stretching vibration modes, respectively.

The number-average molecular weight, M_n , and the polydispersity, M_w/M_n , of the block copolymers were evaluated with the GPC, as listed in Table 1. The copolymers in THF have a dendron aromatic ring absorption band at 212 nm. The molar extinction coefficient (182,000 M⁻¹ cm⁻¹) of the 212 nm band of 3,5-bis(3,5-bis(benzyloxy)benzyloxy)benzyl bromide in dilute THF solution was determined using the Lambert-Beer law and was utilized to calculate the number of dendrons per copolymer, i.e., the degree of polymerization, *l*, of a PD₃MA block (Table 1). From the elemental analysis, the C-to-H molar fraction of the

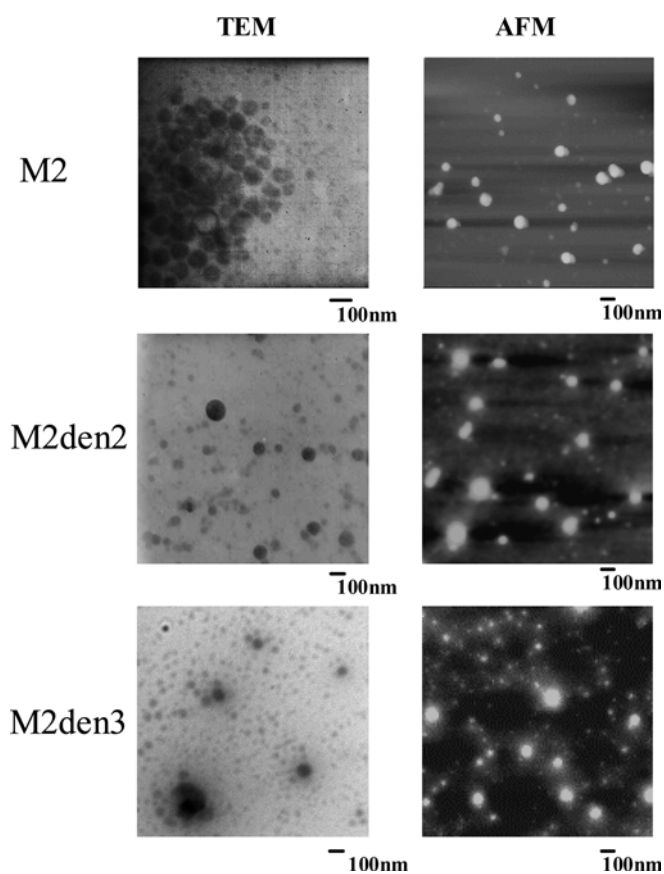


Fig. 2 Transmission electron microscope (*TEM*) and atomic force microscope (*AFM*) images of films cast from chloroform solutions of block copolymers

copolymers was obtained (Table 1). From the values of M_n and the C-to-H molar ratio, the degrees of polymerization of PMAA and PFA were calculated, as listed in Table 1. Consequently, the dendron was replaced in 3/58 portions of the PMAA block in

M2den1, 2/3 in M2den2 and 28/30 in M2den3. The rich replacement to the dendron made us expect an increase in the rigidity of the copolymer structure because of the compactness of the dendron side chain in addition to the rigidity of the fluorocarbon side chain. Estimated molecular lengths are included in Table 1. The backbone main chains of the copolymers cannot take on a trans-zigzag configuration because of steric hindrance of the side chains, i.e., bulky dendron and rigid PFA, but in a trans-gauche-type configuration, the distance between side chains is wider than the thickness or the diameter of the side chains. Therefore, when the chain structures of the copolymers were approximated by the trans-gauche-type configuration, the molecular length [P(D₃MA,MAA) block length a plus PFA block length b] was estimated by multiplying the degree of polymerization by 2.17 Å, which is one pitch length of a repeating unit. Such a configuration of the main chain was already estimated for PMMA-*b*-PFMA [22]. As seen in Table 1, the evaluated lengths of the copolymers are only 8–13 nm.

Association in solution and at the interface

The intensity of the UV-vis band (212 nm) of THF solutions of P(D₃MA,MAA)-*b*-PFA deviates from the Lambert-Beer law at higher concentrations, indicating the formation of aggregates. The association of copolymers was examined in chloroform. The TEM photographs of cast films prepared from chloroform solutions of PMMA-*b*-PFA (M2) and P(D₃MA,MAA)-*b*-PFA (M2den2, M2den3) are shown in Fig. 2. The three copolymers all formed polydisperse, spherical particles. Similar textures were also obtained from AFM images (Fig. 2). This suggests that the association behavior of the copolymers in chloroform is similar and is not affected by the substitution with the dendron. Since the three

Fig. 3 Surface pressure-molecular area isotherms of Langmuir films of block copolymers

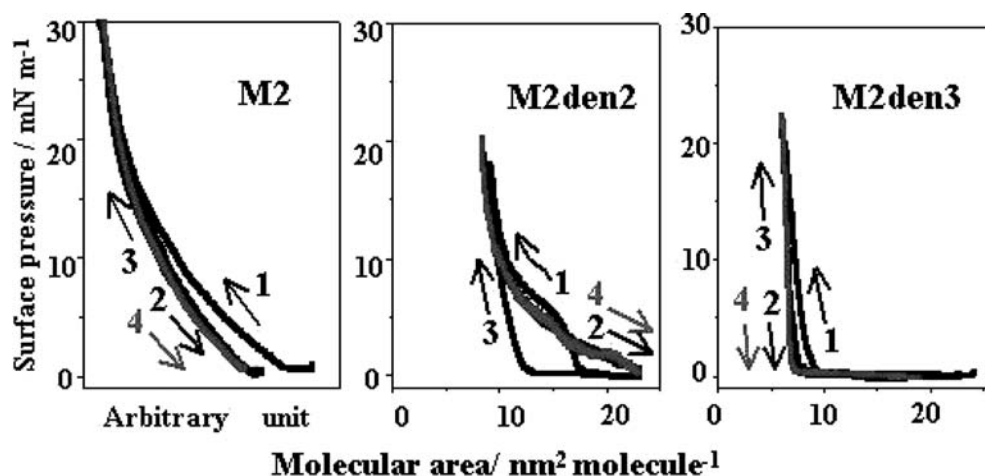


Fig. 4 Brewster-angle microscope images of an M2den3 Langmuir film at different surface pressures

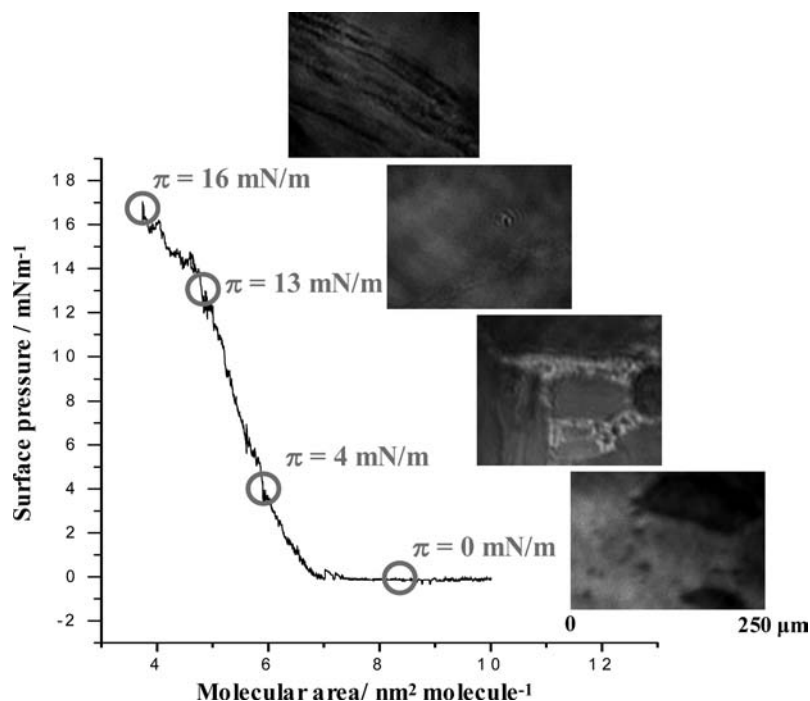
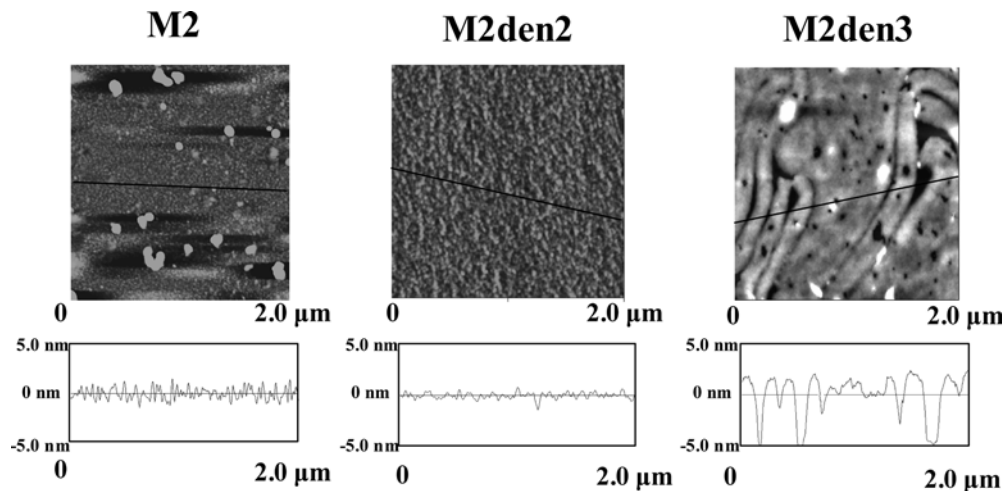


Fig. 5 AFM images of Z-type Langmuir–Blodgett films of block copolymers and their section analyses



copolymers consisted of solvophobic and solvophilic blocks, they all can easily form amphiphilic aggregates like micelles.

The surface area of the Langmuir film of the copolymer at the air/water interface was constantly compressed at a rate of 5 mm min^{-1} . After the liquid and solid states had been observed, the Langmuir films collapsed at a certain surface pressure, which changes with the degree of substitution of the dendron, although the collapse pressure for each copolymer changes with the width owing to the worse reproducibility of the surface pressure–area isotherms, as listed in Table 1. The hysteresis curves of the surface pressure–area isotherms of the copolymers are shown in Fig. 3. On the Langmuir

films of M2 and M2den3, the isotherms after the first expansion curve passed on the same curves. This indicates that the molecular orientation at the first compression remains in the following processes. Remarkable hysteresis was observed on the isotherms of an M2den2 film. They were different not only for the compression and expansion processes of the first turn but also for the compression processes of the first and second rounds. This hysteresis behavior suggests that the molecular orientation in the film arranged at the first compression is somewhat released at the expansion and that the more compact molecular orientation at the following compression is also released in the next expansion process. At the higher turn, the area for the liquid state is diminished,

although the surface area for the solid state remains constant. This behavior should be a characteristic of a moderately dendron substituted block copolymer.

The molecular areas occupied for liquid and solid states on the second compression scan are listed in Table 1. The occupied molecular area of M2 was not determined, because M2 slightly dissolved in chloroform and the molecular area was not accurately determined. Since the occupied area of the solid state on the M2den2 Langmuir film is close to the expected area [the cross-sectional area (about 12.6 nm²) of the P(D₃MA,MAA) block], it seems to be a reasonable value for the copolymer orientation, where the molecular axes orient with almost vertical close packing at the air/water interface. The occupied area of the M2den3 film is smaller than the expected area, if the axes of the molecules are almost vertically arranged at the interface. This suggests the overlap of molecules or the interdigitation of side chains at the interface.

Brewster-angle microscope images of an M2den3 Langmuir film at the first compression scan are shown in Fig. 4. At a surface pressure of 0 mN m⁻¹, many domains of different sizes spread on the water subphase. As the surface pressure was increased, the separated domains gathered and combined. The film had some defects at 4 mN m⁻¹ but grew to be homogenous at 13 mN m⁻¹, and then collapsed at 16 mN m⁻¹. AFM images of Z-type LB films are shown in Fig. 5. The height roughness of the LB film was about 2 nm for M2 and 1 nm for M2den2, which are only 15% and 10% of a molecular length, respectively, indicating the flat surface of the Z-type LB film. The AFM image of the M2den3 film was very different from that of the other two copolymers. M2den3 formed the zone structure, where there were some cracks on and between the zones. The height of the zone was about 7 or 8 nm, which corresponds to the molecular length.

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