

SHORT COMMUNICATIONS

Monolayers from Graft Copolymers Having Uniform Molecular Weight Branches

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In previous papers, we described the surface modification of polymeric materials by using the surface excess phenomenon of added amphiphilic graft copolymers in the polymeric materials.^{1,2} In a polymer matrix, the graft copolymers can accumulate at the surface with the functional comonomer segments under certain environment condition. This surface accumulated layer may be stabilized by the anchor segments in the graft copolymers which are compatible with the matrix polymers thereby providing permanent modification of a polymer surface. In this paper, we have tried to deposit a graft copolymer monolayer onto a commodity polymer surface to modify the surface properties as an alternative surface modification method. It is well-known that the surface properties of materials such as wettability can be dramatically changed by a deposition of a monomolecular layer of other compounds.^{3-5,10} Monolayers of graft copolymers as well as block copolymers having anchor segments can be expected sufficiently stable and tenacious to the substrate surface compared to the monolayer of the usual amphiphiles or lipids, thus suit-

able for surface modification. Furthermore, the surface structure of the modified surface is more definite and can be expected to be precisely controlled to achieve the molecular coating by this method. This study also provides the useful information about the structure and role of the surface layer of the previous method where the detailed structure of the surface accumulated layer of graft copolymers is not well understood at present.

Poly(2,3-dihydroxypropyl methacrylate-*g*-styrene) (GDS) and poly(methacrylic acid-*g*-styrene) (GAS) were prepared by radical copolymerization of styrene macromonomers of a narrow molecular weight distribution with isopropylidene-glycerol methacrylate (IPGMA) and methacrylic acid (MAA), respectively. The number and length of branch segments were controlled by the molecular weight and feed composition of the corresponding macromonomer. The number-averaged molecular weight of PSt branch segments (M_n^b) are 5400 and 12400. IPGMA monomer units in the graft copolymers were converted to 2,3-dihydroxypropyl methacrylate (DHPMA) by hydrolysis with trifluoroacetic acid. The charac-

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Table I. Characterization of graft copolymers

Sample code	$M_n \times 10^{-3}$ *		Number of graft	Composition/wt%**	
	Total	M_n^b ***		Macromonomer	Comonomer
GAS-4	1460.0	12.4	19.1	16.2	83.8
GAS-2	495.3	12.4	16.0	40.1	59.9
GAS-6	277.7	12.4	13.6	60.8	39.2
GDS-8	89.9	5.4	2.1	12.3	87.7
GDS-9	101.1	5.4	3.2	17.0	83.0
GDS-11	79.6	5.4	6.7	45.1	54.9
GDS-15	69.5	12.4	2.7	48.3	51.7

* Determined by GPC and membrane osmometry.

** Determined by ^1H NMR and elementary analysis.

*** Number-average molecular weight of PSt branch.

teristics of these graft copolymers are shown in Table I. The details of preparation and characterization including the swelling behavior of these graft copolymers in water were described previously.^{6,7} These amphiphilic graft copolymers are swellable but insoluble in water, accordingly, can be expected to spread on water surface to form a monolayer using an adequate spreading solvent.

Mixed solvents of benzene (Bz), tetrahydrofuran (THF), and methanol were used as spreading solvents. The concentration of the spreading solution was typically 5×10^{-4} g ml $^{-1}$. 150–400 μl of the solution was placed dropwise manually from a microsyringe and spreaded on water surface. Surface pressure–area (π – A) curves were measured by using a Wilhelmy-type surface pressure meter of Kyowa Kaimenkagaku Co., Ltd., Japan (HMB-AP2). The surface area of the trough was 100 cm 2 . The glass plates were used as the Wilhelmy plate, the thickness and width of which were 24 mm and 0.3 mm. The compression speed was typically 5 mm min $^{-1}$ (7.5 cm 2 min $^{-1}$). The surface pressure values were read at each compression step by advancing the movable Teflon barrier at room temperature ($23 \pm 1^\circ\text{C}$). Twice distilled water was used after passing through an active charcoal column.

The graft copolymer layers on the water

surface were transferred onto the PSt substrate by touching the PSt surface to the monolayer at the air–water interface from upside. Contact angle measurements were carried out to examine the surface properties of the graft copolymer deposited substrate using a CA-A type goniometer of Kyowa Kaimenkagaku Co., Ltd.

Figure 1 shows typical π – A curves of GDS-11 and 15 in compression, M_n^b of which are 5400 and 12400, respectively. The horizontal axis in the figure represents the area per hydrophobic PSt graft chain. From this figure, the limiting area (A_0) obtained by extrapolating the linear region of the π – A curve below the inflection to horizontal axis ($\pi=0$) is 4.45 nm 2 /branch for GDS-11 and 9.66 nm 2 /branch for GDS-15. A_0 values of graft copolymers are summarized in Table II together with the spreading conditions. Although there were some hysteresis in π – A curves, obtained A_0 values in compression were almost reproducible under the same experimental conditions. The thickness (d) of PSt layer at $A=A_0$ was also estimated assuming the density (ρ) of PSt layer equal to that of bulk PSt and shown in Table II.

In Figure 2, A_0 values are plotted against M_n^b with the data of graft copolymers and block copolymers of poly(vinyl alcohol)–polystyrene and poly(vinyl acetate)–polystyrene reported by Ikada *et al.*⁸ The solid

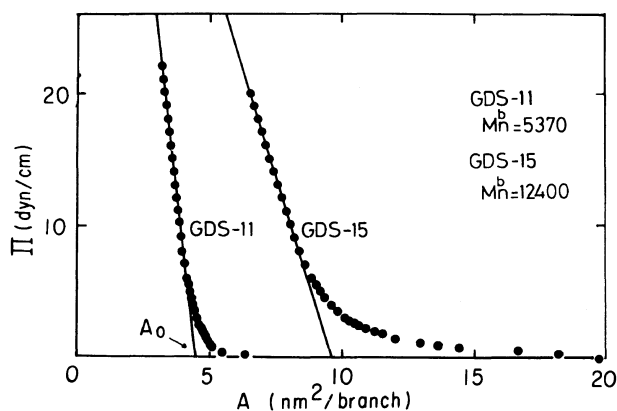


Figure 1. π - A curves of graft copolymers GDS-11 and GDS-15 at room temperature. Horizontal axis is the close sectional area per PSt branch. The limiting area, A_0 , is defined as indicated.

Table II. Spreading condition and limiting area of amphiphilic graft copolymers on water surface^a

Sample code	Spreading solution			Limiting area (A_0) m ² g ⁻¹	A_0 per branch nm ²	$A_0^{1/2}$ nm	d nm	
	Mixing ratio (Bz: THF: MeOH)	Concn (10 ⁻⁴ g ml ⁻¹)	Amount μl					
GAS-4	2:4:4	5.1	300	107	13.6	av. 14.3	3.8	1.4
	2:4:4	4.9	300	118	15.1			
GAS-2	1:6:3	5.0	300	172	8.8	av. 10.1	3.2	1.9
	2:5:3	5.0	150	217	11.5			
GAS-6	2:5:3	5.0	300	199	10.2	av. 8.5	2.9	2.3
	2:5:3	5.1	300	248	8.4			
GDS-8	2:5:3	5.1	300	250	8.5	av. 6.6	2.6	1.3
	2:5:3	5.1	300	258	8.7			
GDS-8	1:2:7	5.1	400	81.5	5.9	av. 6.6	2.6	1.3
	1:2:7	5.1	300	109	7.9			
GDS-9	1:4:5	5.2	250	89.3	6.5	av. 6.1	2.5	1.4
	1:4:5	5.2	250	88.9	6.4			
GDS-9	1:4:5	5.2	250	89.0	6.5	av. 6.1	2.5	1.4
	2:4:4	5.0	300	124	6.5			
GDS-11	2:4:4	5.4	300	112	5.9	av. 4.7	2.2	1.9
	2:4:4	5.4	300	115	6.0			
GDS-11	2:4:4	5.4	300	225	4.5	av. 4.7	2.2	1.9
	2:4:4	5.6	300	241	4.8			
GDS-15	2:4:4	5.4	300	250	4.9	av. 8.9	3.0	2.2
	2:4:4	5.6	300	227	9.7			
GDS-15	2:4:4	5.6	300	205	8.7	av. 8.9	3.0	2.2
	2:4:4	5.1	300	197	8.4			

^a Surface pressures were measured by Wilhelmy-type surface pressure meter at room temperature.

line in the figure corresponds to the $A_0 = \pi(3M_n^b/4\pi\rho N_A)^{2/3}$ assuming ρ to be equal to the density of bulk PSt, where N_A is Avogadro number. It is seen in Figure 2 that

these A_0 versus M_n^b relationships are almost identical with respect to the PSt segment irrespective of the difference of backbone component and copolymer structure. This provides

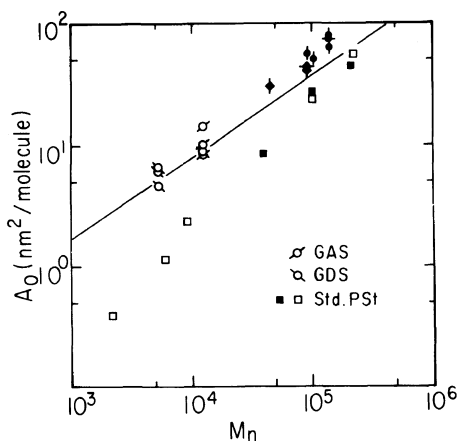


Figure 2. Limiting area (A_0) occupied by one PSt branch *versus* molecular weight of the PSt branch (M_n^b) plots. Open symbols were measured in this study and closed symbols were plotted from ref. 8. (\circ), (\square), (\blacksquare), and (\square) are as indicated in the figure. (\bullet) PVAc-PSt graft copolymers; ($\text{---}\bullet\text{---}$) PVA-PSt graft copolymer; (\blacklozenge) PVAc-PSt block copolymers; ($\text{---}\blacklozenge\text{---}$) PVA-PSt block copolymer.

a good indication of the formation of monolayers in our graft copolymer system where the monodisperse molecular weight PSt graft segments cover the water surface by two-dimensional packing of dense spherical PSt particles while the hydrophilic backbone segments swell with or dissolve into water. Accordingly, M_n^b is predominantly responsible for A_0 while the total molecular weight has almost no correlation with A_0 . A_0 *versus* M_n relationship of standard PSt samples was also measured with the same procedure and shown in Figure 2 for comparison. In the case of homopolymers, A_0 is smaller than that of copolymers at the same M_n . A_0 becomes much smaller as the M_n of PSt decreases. This result is consistent with that of Ikada *et al.*⁸ but lower than that reported by Kumaki,⁹ clearly due to the aggregated and multilayer structure of PSt surface films. Thus, the hydrophilic segments play an important role in the formation of a monomolecular layer.

It is seen in Table II that A_0 values of GAS samples increase as the content of PSt branch

component (W_{st}) decreases in spite of these GAS graft copolymers having the same M_n^b . This is presumably due to the contribution of the MAA backbone segment in the π - A curve. The contribution from hydrophilic backbone segment on A_0 is more clearly seen by comparing the thickness of PSt layer with $A_0^{1/2}$ in Table II. When the content of the PSt branch component is high (GAS-6, GDS-11, and GDS-15 in Table II), $A_0^{1/2}$ is larger but close to the corresponding d value. However, $A_0^{1/2}$ values are much larger than d in the case of GAS-4, GAS-2, GDS-8, and GDS-9, where W_{st} are low (the values in wt% are 16.2, 40.1, 12.3, and 17.0, respectively). In these cases, the contribution from the backbone to the surface pressure might be considerable. The more pronounced effect of the backbone segment in GAS than in GDS in Table II can be ascribed to the fact that the solubility of MAA segments in water is less than DHPMA segments in this study since the dissociation constant of carboxylic groups under neutral condition is small.

The monolayer films of GDS-9 at air-water interface thus obtained were deposited on PSt substrate at different surface pressures. Contact angles of water droplets on the graft copolymer deposited PSt were measured to examine the alternation of the polystyrene surface by the deposition. It was found that the contact angle of water on PSt substrate much decreased by the deposition of a graft copolymer layer. It tended to decrease with increase of the surface pressure at which the deposition was carried out. Further study on the monolayers of the graft copolymers and the surface properties of the PSt substrate deposited by the monolayer are now in progress. The results will be compared with those of the PSt surface modified by surface accumulation of the same graft copolymers.²

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