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Monolayer of Polystyrene Monomolecular Particles on a Water Surface Studied by Langmuir-Type Film Balance and Transmission Electron Microscopy[†,1]

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ABSTRACT: The behavior of a monolayer of polystyrene monomolecular particles which was obtained by spreading dilute solutions in benzene on the water surface was studied by a Langmuir-type film balance and transmission electron microscopy (TEM). Since polystyrene has no hydrophilic group, the surface pressure measured by the film balance was not due to the real decrease of the surface tension but due to a mechanical force by compression, thus the π–A curves were apparent π–A curves. However, the macroscopic observation by the film balance was in good agreement with the microscopic observation by TEM, indicating the particles are stable against the compression. At the limiting area, A_0, the monomolecular particles covered 56% of the water surface, but they could not be most closely packed by further compression. In addition to the higher molecular weight samples, apparent π–A curves were measured for lower molecular weight samples, for which formation of monomolecular particles has not been confirmed because of the limited resolution of TEM; the observed small A_0 indicated the particles were not formed or were unstable against the compression.

I. Introduction

Polymer monolayers that are spread on the water surface have been widely studied, including both synthetic polymers and biopolymers.[2–4] Polymers with sufficient hydrophilic groups in the repeating unit, such as poly(vinyl acetate),[5] are well-known to be ideal monolayers on the water surface with every repeating unit being absorbed on the water surface.

In contrast polymers without hydrophilic groups in the repeating unit, such as polystyrene[6–8] and poly(vinyl chloride),[3] do not spread to be monolayers on the water surface because of the lack of the sufficient affinity to water. The surface pressure–area curves (π–A curves) of these polymers show extraordinarily small limiting areas compared with their molecular structures, indicating the polymers exist on the water surface as flakes or multilayers. Recently we studied polystyrene spread films on the water surface from dilute solutions in benzene by transmission electron microscopy (TEM) and found that if the concentration of the solution is dilute enough (about 2×10^{-6} g/mL), polystyrene monomolecular particles, each of which contains one molecule, were obtained on the water surface.[9]

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The particles were identified to be monomolecular mainly by detailed studies on the diameter distributions of the particles.

In this paper the behavior of a monolayer of the particles was studied by π–A curves and TEM, and these macroscopic and microscopic results were compared. In addition to those for the higher molecular weight polystyrenes, π–A curves were measured for lower molecular weight samples, for which formation of monomolecular particles has not been confirmed because of the limited resolution of TEM; the possibility of the formation of monomolecular particles at this low molecular weight regime was discussed.

II. Experimental Section

Commercially available polystyrenes of narrow molecular weight distributions for GPC calibration were used. Weight-averaged molecular weight (M_w) 3.84×10^6, 4.48×10^6, 5.48×10^6, 6.77×10^6, 8.42×10^6 ($M_w/M_n < 1.17$), and 2.06×10^7 polystyrenes were purchased from Toyo Soda (Japan). Nominal molecular weight 4000, 1.75×10^4, 6.0×10^5, and 9.5×10^5 ($M_w/M_n < 1.1$) polystyrenes were purchased from Pressure Chemical Co. Nominal molecular weight 800, 8.5×10^3, 5.0×10^4, 1.0×10^5, 4.7×10^5, and 2.3×10^6 polystyrenes were purchased from Waters Associates. Nominal molecular weight 1050 ($M_w/M_n < 1.2$), 1200, 1770, and 2470 ($M_w/M_n < 1.08$) polystyrenes were purchased from Polymer Laboratories.

Special grade benzene for fluorescent measurement was used after distillation. Water was distilled twice from a quartz still. The glass apparatus was etched with concentrated KOH–ethanol solution and thoroughly rinsed with doubly distilled water. A commercial Langmuir-type film balance (Lauda Film Balance) was used as a trough.

Polystyrene solutions were spread on the water surface as follows. A drop of dilute solution was placed on the water surface by using a Teflon syringe. After a drop of benzene was spread and evaporated, another drop was added. By repeating this, a prescribed amount of the solutions was spread. In order to obtain monomolecular particles, quite dilute solutions have to be spread on the water surface. In the case of M_w 3.84×10^6 polystyrene, the concentration of the solutions should be below 2×10^{-6} g/mL to obtain almost only monomolecular particles.[9] Thus large amounts of solution have to be spread to obtain a sufficient amount of particles to measure π–A curves. Typically 0.2 mL of solution was spread for 2×10^{-4} g/mL solutions, 2 mL for 2×10^{-5} g/mL solutions, and 20 mL for 2×10^{-6} g/mL solutions, respectively. The first and second were spread manually. The last was spread by the use of an automatic feeder, which compresses attached syringes at a constant rate; typically two Teflon syringes (50 mL each) were attached and compressed at a rate of 2 mL/h.

Usually π–A curves were measured by the Langmuir-type film balance (LAUDA film balance) by compressing the area at a rate of 15 cm^2/min; the temperature of the subphase was 20 °C. π–A curves by Wilhelmy method were measured with a Wilhelmy-type surface pressure measuring unit (MJF-2, Kyowa Kaimenkagaku Co., Ltd., Japan) which was attached to the LAUDA film balance. The Wilhelmy plate was placed in front of the original Langmuir-type surface pressure measuring unit of LAUDA. The plate was platinum of thickness 0.15 mm and width 20.2 mm.

The particles were transferred onto TEM copper grids which were covered with collodion films reinforced with evaporated carbon, by touching the grid surface to the water surface (the horizontal lifting method). The particles were observed by TEM without further treatment such as staining or observed after shadowing with platinum–carbon. The shadowing angle was about 13°.

III. Results and Discussion

1. Comparison between π–A Curves and TEM Results. Figure 1 shows a typical π–A curve of monomolecular particles from a polystyrene of molecular weight 6.77×10^6.[1] On compression, the surface pressure was monotonously increased. Qualitative shapes of the π–A curves were almost the same as those reported previously.[6-8] The limiting area A_0, which is defined by extrapolating the maximum slope of the π–A curve to zero surface pressure as indicated in the figure, was 3.6×10^5 A^2/molecule. On the other hand, the number-averaged area of the monomolecular particles determined by the direct observation by TEM, A_{TEM}, was 2.0×10^5 A^2/molecules. Areas determined both by the macroscopic observation (A_0) and by the microscopic observation (A_{TEM}) are of the same order. The ratio of A_{TEM}/A_0, which indicates the ratio of the area occupied by the monomolecular particles to the overall area at A_0, is 56%.

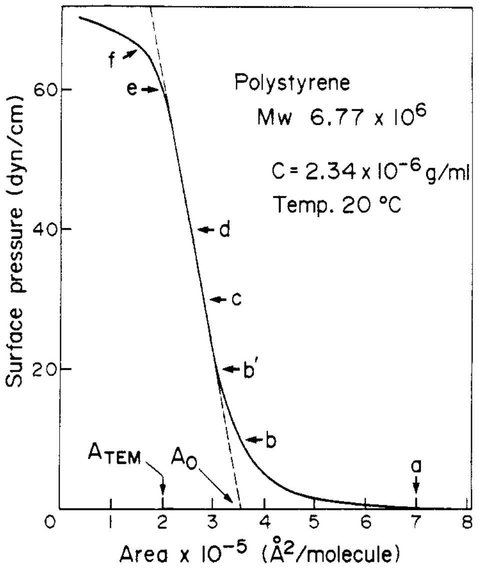

Figure 1. π–A curve of polystyrene monomolecular particles of $M_w = 6.77 \times 10^6$. As polystyrene has no hydrophilic group, the surface pressure measured is not a true surface pressure but an apparent one. This is the same case for other figures. The origin of this apparent surface pressure will be discussed in section III-3. The limiting area, A_0, is defined as indicated. A_{TEM} is the number-averaged area of the monomolecular particles determined by TEM. The eight arrows (a–f) indicate areas where the particles were transferred for TEM observation (Figures 2 and 3).

Figure 2 shows TEM pictures of the monomolecular particles which were transferred at the areas indicated in Figure 1. Here A is the area per molecule, at which the particles were transferred. From A_{TEM}/A, the TEM pictures, for example, Figure 2a,c, are estimated to contain about 1600 and 7200 particles, respectively. Although some extraordinarily large particles exist in Figure 2a,e, the number of them is quite small compared with that of monomolecular particles, indicating the monomolecular particles formed quite well.

Even at $A_{\mathrm{TEM}}/A = 29\%$, the monomolecular particles are in contact with each other. On compression, the particles become more densely packed, and at $A_{\mathrm{TEM}}/A = 77\%$ (30 dyn/cm) in part high contrast areas were observed, indicating the monolayer film of the monomolecular particles began to collapse. But in this stage the size of the collapsed area correspond to one particle. After further compression, at $A_{\mathrm{TEM}}/A = 110\%$ (60 dyn/cm) and $A_{\mathrm{TEM}}/A = 130\%$ (66 dyn/cm), the film was considerably collapsed and the size of the collapsed areas reached several to ten particles. At this stage the collapse of the monomolecular particle film on the water surface became visible. Even at the surface pressure as high as 60 dyn/cm ($A_{\mathrm{TEM}}/A = 110\%$), there are vacant spaces in the film.

Figure 3 shows TEM pictures of the monomolecular particles shadowed by platinum–carbon simultaneous shadowing after they were transferred at different compression stages indicated in Figure 1. The shadowing angle was about 13°. The collapsed areas, which were high

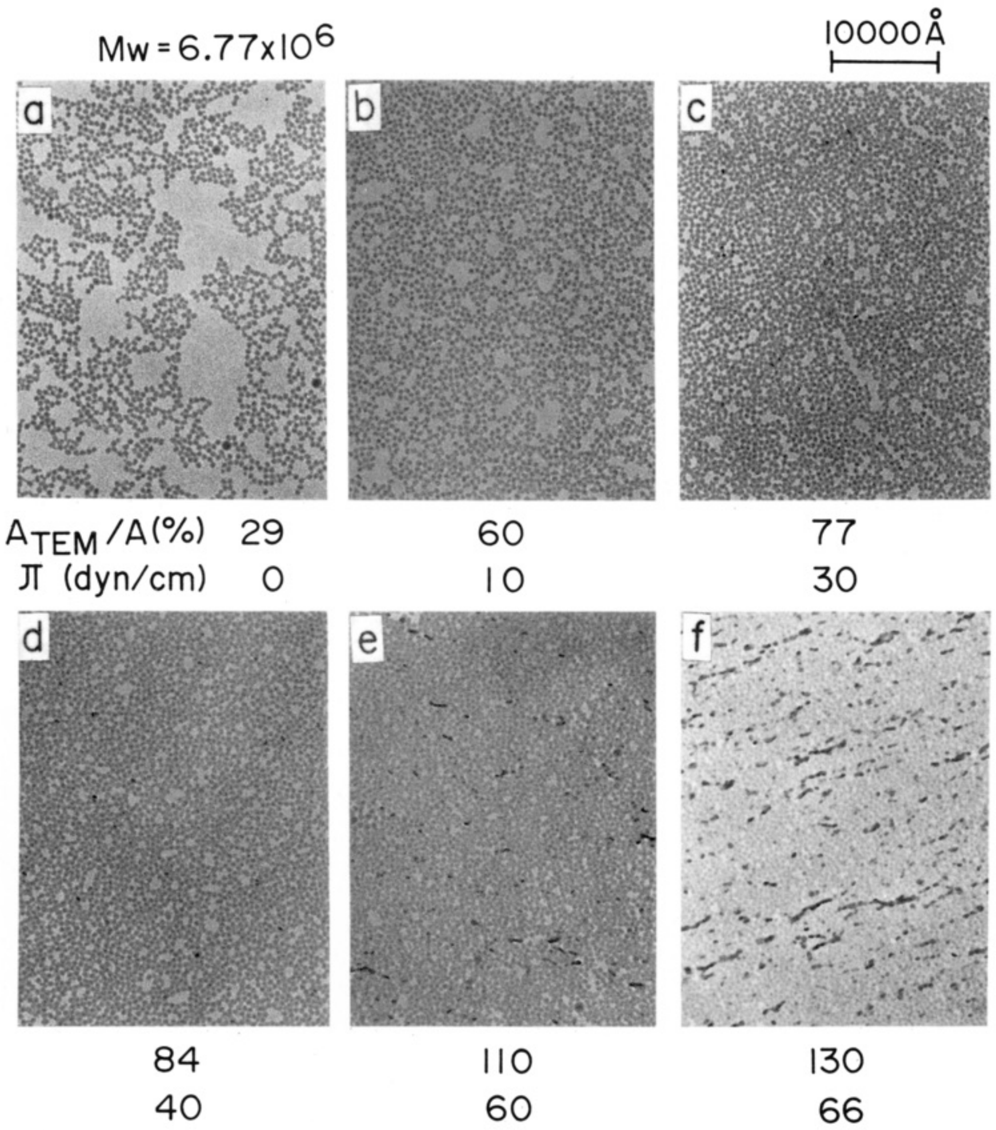

Figure 2. Transmission electron micrographs of polystyrene monomolecular particles transferred at different compression states indicated in Figure 1. The number-averaged diameter of the particles was 508 Å.[9] *A* is the area per molecule at which the particles were transferred.

contrast areas in Figure 2, correspond to the stacked particles on the relatively close packed particles. Since the particles were transferred by the horizontal lifting method, the surface observed in Figure 2 was in contact with the water when it was on the water surface.

As have been mentioned above, the result of the macroscopic π–A curves and the microscopic TEM observation are in good agreement, but in order to obtain monomolecular particles, the concentration of the solution must be very dilute (about 2×10^{-6} g/mL), thus a large amount of the solution has to be spread on the water surface. Therefore small amounts of nonvolatile impurity which may exist in the solvent may not be negligible. Figure 4 shows the result of the blank tests of the benzene along with the π–A curves of polystyrenes. The solid line indicates the case of the 2.34×10^{-6} g/mL solution; the broken line indicates that of the 2.56×10^{-5} g/mL solution. Even in the case of the benzene only, surface pressure increased. The area closed by the π–A curves has dimensions of energy and is considered to be the energy which is necessary to collapse the surface film on the water. The ratio of the energy, polystyrene/impurity in benzene, is 1/0.1 (2.34×10^{-6} g/mL) and 1/0.01 (2.56×10^{-5} g/mL). Thus the film of the monomolecular particles obtained from the 2.34×10^{-6} g/mL solution is a mixed film of polystyrene and impurities in benzene (about 10%). In the case of 2.56×10^{-5} g/mL solutions, the impurities in benzene are almost negligible. The limiting area, A_0, from the 2.56×10^{-5} g/mL solution is 2.6×10^5 Å^2/molecule, which is 29% smaller than that from the 2.34×10^{-6} g/mL solution; this decrease is in part due to the decrease of the impurity and in part due to the increase of the ratio of multimolecular particles to the monomolecular particles.[9] Thus the precise limiting area of the monomolecular particles should be between the two values.

As more precise values were difficult to obtain, subsequent experiments were carried out by using solutions of about 2×10^{-5} g/mL concentration; although the particles from them contain multimolecular particles, the impurity of the solution is almost negligible.

2. The Irreversibility of the π–A Curves. Because of the lack of hydrophilic groups in polystyrene, the π–A curves shown in Figures 1 and 4 are not true π–A isotherms but represent the irreversible compression behavior of the particle arrangements.

Figure 5 shows a π–A curve measured as follows. At first the particles were compressed to the surface pressure 35 dyn/cm (broken line), then expanded to the area of 5.2×10^5 Å^2/molecule, and again compressed to be collapsed (solid line). The rate of both the compression and the

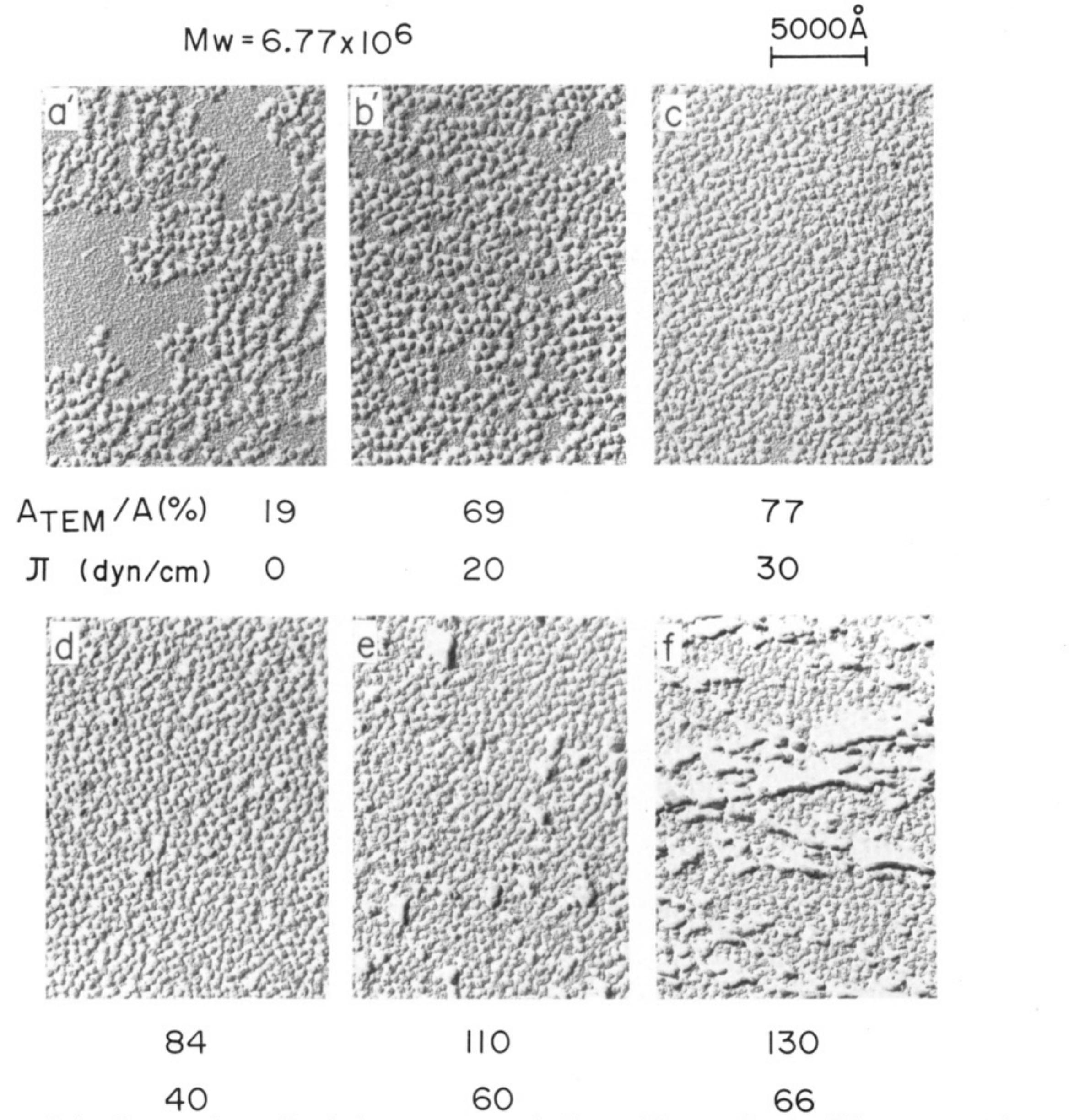

Figure 3. Transmission electron micrographs of polystyrene monomolecular particles, transferred at different compression states indicated in Figure 1. The particles were shadowed with platinum–carbon at an angle of about 13°.

expansion was 15 cm^2/min. The surface pressure at the second compression was lower than that of the first compression, thus the once compressed film did not spread by the subsequent expansion, indicating the compression is irreversible.

The π–A curve at the second compression intersected that of the first compression at the surface pressure 35 dyn/cm, then bent at that point, and went up on the extrapolated line of the first π–A curve, as if the film had been compressed continuously without the expansion. This behavior is similar to that of plastic deformation. This plastic deformation like behavior is not due to the deformation of the particles themselves, it indicates the aggregated structures of the particles at 35 dyn/cm, which are similar to those shown in Figure 2c,d, did not change even after the expansion; this is reasonble because polystyrene has no hydrophilic groups and there is no repulsive force which breaks the contacts of the particles.

3. Origin of the Surface Pressure. Since polystyrene has no hydrophilic group in the repeating unit, the origin of the surface pressure measured by the film balance is not clear. A Langmuir-type film balance measures the force working on the float which divides the water surface covered with molecules from a pure water surface.[10] Thus if only a mechanical force works on the float without decrease of the surface tension, an apparent increase of the surface pressure will be observed. On the other hand the Wilhelmy-type film balance measures the surface tension directly, the mechanical force will not be observed as an apparent surface pressure.[10] In order to understand the surface pressure measured by the Langmuir-type film balance, π–A curves were measured by the Wilhelmy-type film balance.

Figure 6 shows these π–A curves: (a) measured by the Langmuir-type film balance; (b),(c) measured by the Wilhelmy-method; the Wilhelmy plate was vertical (b) and parallel (c) to the compression direction, respectively. Surface pressure measured by the Wilhelmy method was smaller than that by Langmuir method. In the case of the Wilhelmy plate vertical to the compression direction (b), on compression the contact angle on the plate at the moving barrier side, which was originally zero, increased and finally became almost 90°; in contrast that on the opposite side (the Langmuir-type surface pressure meas-

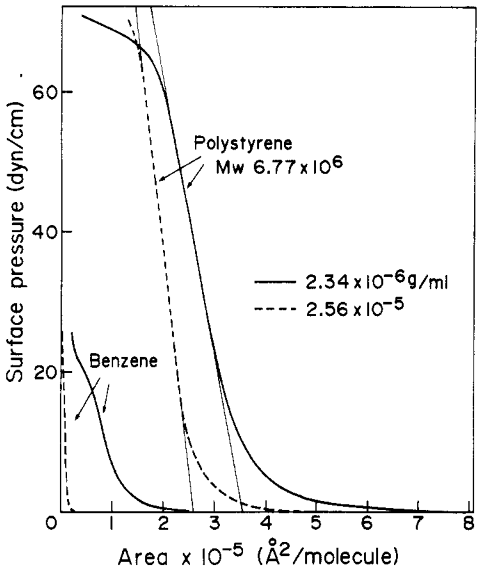

Figure 4. π–A curves of polystyrene along with the blank tests of benzene. The solid line represents the case of a 2.34×10^{-6} g/mL solution. The broken line represents that of a 2.56×10^{-5} g/mL solution.

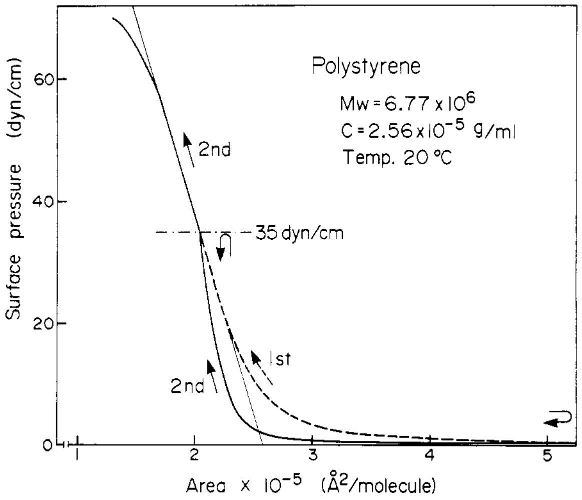

Figure 5. π–A curve of polystyrene, measured by compressing to 35 dyn/cm (broken line, first), then expanding to 5.2×10^5 Å^2/molecule, again compressing to be collapsed (solid line, second).

uring unit side) did not change. Thus surface tension did not work at the moving barrier side, this is considered to be the reason for the increase of surface pressure observed. The maximum surface pressure was 34 dyn/cm, which is about a half of the surface tension of the pure water surface (72.8 dyn/cm, 20 °C); this is consistent with the above consideration. The increase of the contact angle at the moving barrier side was probably due to deposition of the polystyrene on the plate. In the case of (c), for the plate parallel to the compression direction, the surface pressure was lower (11 dyn/cm). The contact angle did not increase significantly during compression. The apparent surface pressure is probably due to the same contamination. The limiting areas measured by the both methods were almost the same.

As mentioned above, surface pressures measured by the Langmuir-type film balance were concluded to be mainly due to the mechanical force of the compression. The effective length of the float of the Lauda Film Balance is 12 cm. If the thickness of monomolecular particle film on the water surface is assumed to be 40 Å, a surface pressure of 60 dyn/cm corresponds to 1.5×10^7 Pa (148 atm). Similarly the compressibility of the monomolecular particle film in Figure 1, 7.8×10^{-3} cm/dyn, corresponds to 3.1×10^{-8} Pa^{-1}, which is 1/141 of that of the bulk polystyrene (2.2×10^{-10} Pa^{-1}).[11] Therefore the mechanical force which works on the monomolecular particles on the water surface is much smaller than the force which is necessary to deform the particles; thus almost all the particles in Figures 2 and 3 were not deformed considerably after the collapse of the film.

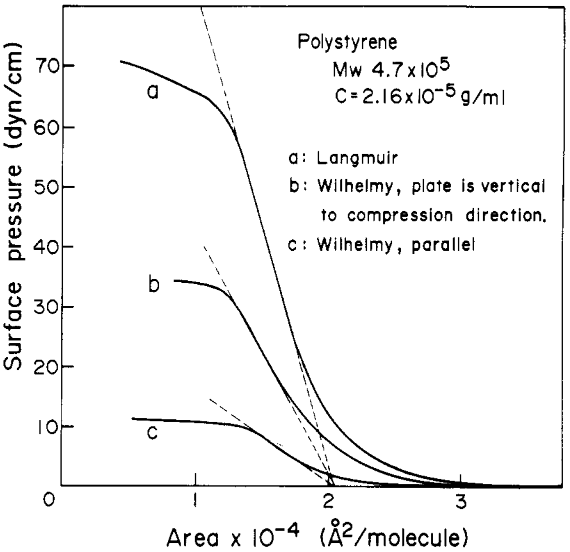

Figure 6. π–A curves measured by the Langmuir method (a) and by the Wilhelmy method (b), (c). The Wilhelmy plate was vertical (b) and parallel (c) to the compression direction.

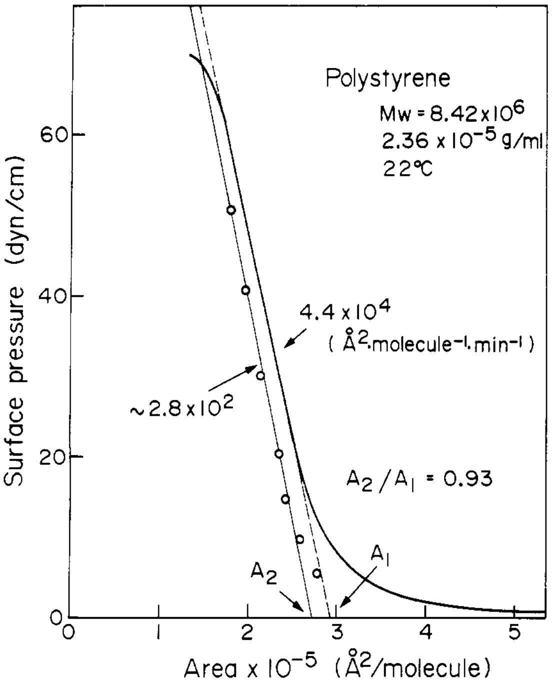

Figure 7. Dependence of π–A curves on the compression rates. Solid line: π–A curve measured by the usual compression rate, 4.4×10^4 Å^2 molecule^{-1} min^{-1}. Open circles: π–A curve measured by a stepwise compression, details are shown in the text; the compression rate was 2.8×10^2 Å^2 molecule^{-1} min^{-1}.

4. Dependence of the π–A Curves on the Compression Rate. In the case of such an irreversible compression, π–A curves may depend on the compression rate. Figure 7 shows the dependence of the π–A curve on the compression rate. The solid line is a π–A curve measured at the usual compression rate, 4.4×10^4 Å^2 molecule^{-1} min^{-1} (15 cm^2/min). The open circles were measured as follows. The film was compressed at the same rate; after the

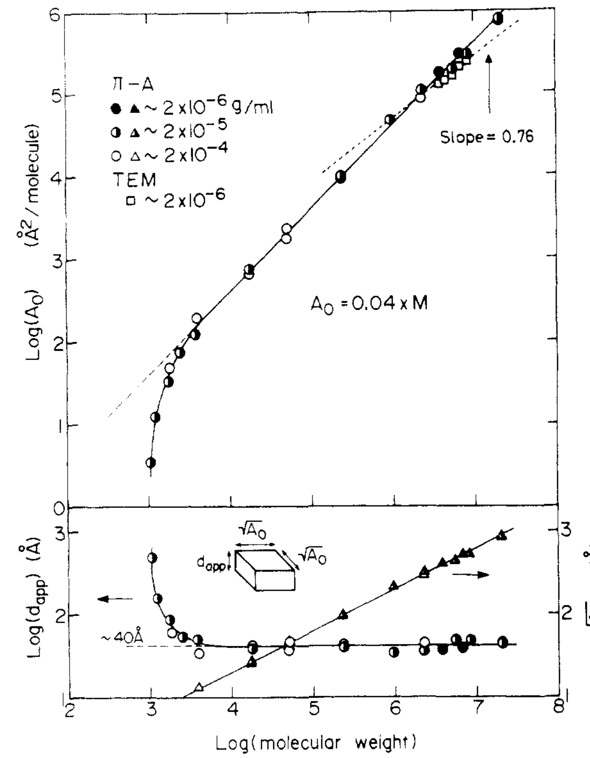

Figure 8. Upper graph: Molecular weight dependence of the limiting areas determined by π–A curves along with the number-averaged areas of monomolecular particles determined by TEM. Lower graph: Molecular weight dependence of the apparent thickness, d_{app}, along with $A_0^{0.5}$. d_{app} was calculated from A_0 by assuming polystyrene films on the water surface were continuous films with the bulk density 1 g/cm^3. d_{app} and $A_0^{0.5}$ correspond to the two sides as indicated in the figure, if a molecule on the water surface is assumed to be a square prism.

pressure became 5 dyn/cm, the film was held at this constant pressure for 1 h; then area was measured; the film was again compressed to the pressure 10 dyn/cm; held for 1 h; and then the area was measured; by repeating this, the π–A curve was obtained. The compression rate corresponds to about 2.8 × 10^2 Å^2 molecule^{-1} min^{-1} (0.1 cm^2/min), which is about 1/160 of that of the usual measurement. The decrease of the limiting area is about 10%, thus the dependence on the compression rate is small. On the basis of this result, the limiting areas obtained at the compression rate of 15 cm^2/min will be discussed.

5. The Molecular Weight Dependence of the Limiting Areas. Figure 8 shows the dependence of the limiting areas, A_0, on the molecular weight. In this log–log plot, the difference of the limiting areas due to the dependence on the solution concentrations is negligible.

For a wide molecular weight range from 4000 to 2.06 × 10^7, the limiting areas are proportional to the molecular weights, and the relation was represented by the empirical equation

$$A_0 = 0.04M \qquad (1)$$

where A_0 is the limiting area per molecule (Å^2/molecule) and M is the molecular weight of the polymer. Equation 1 indicates the limiting area per repeating unit is constant, 4 Å^2/repeating unit, which is much smaller than the area of the molecular structure of polystyrene; thus polystyrene chains are multilayered in particles on the water surface.

At the molecular weights less than 4000, the relation deviates from eq 1 and polystyrene chains are multilayered more considerably. As mentioned above (section III-3), the surface pressure observed in this study is mainly due to the mechanical resistance offered by the particles to compression. At this low molecular weight regime, the surface pressure should be affected by a decrease of the glass transition temperature due to the low molecular weights. Actually a polystyrene of a molecular weight of 800 which is a liquid at room temperature did not show an increase of the surface pressure ($A_0 < 1.3$ Å^2/molecule), indicating the sharp drop in A_0 at this molecular weight regime is due to the decrease of the glass transition temperature of the polymer.

The five open squares in the high molecular weight regime from 3.84 × 10^6 to 8.42 × 10^6 represent the number-averaged areas of the monomolecular particles, A_{TEM}, determined by direct observation in TEM. As mentioned above, both A_0 and A_{TEM} are of the same order. But as reported previously, the dependence of the diameter of the monomolecular particles on the molecular weight was represented by the equation,[9]

$$D = 1.33 \times M^{0.38} \qquad (2)$$

where D is the diameter of the monomolecular particles in angstroms and M is the molecular weight. Thus the relation represented by the equation

$$A_0 \sim M^{0.76} \qquad (3)$$

is expected, by assuming the ratio of the area occupied by the particles to the overall area is independent of the size of the particles. This molecular weight dependence is different from that of eq 1. Equation 3 was derived from only five data points at the molecular weights ranging from 3.84 × 10^6 to 8.42 × 10^6, on the other hand eq 1 was derived for the wider molecular weight regime from 4000 to 2.06 × 10^7. But even at the higher molecular weight regime these two scalings seem to be different. (The dotted line in Figure 8 indicates a scaling of 0.76.) This indicates that the above assumption seems to be not valid; that is, the ratio of the area occupied by the particles to the overall area at A_0 seems to depend on the size of the particles. The packing behavior of the monomolecular particles on the water surface is rather complicated. The particles initially have an aggregated structure before compression. (This structure might be described by a diffusion-limited aggregation mechanism.[12]) By the subsequent compression, the aggregated structure is forced to rearrange; the surface pressure corresponds to the resistance against this rearrangement. As a result, the particle arrangements are determined, which seem to depend on the size of the particle.

If the polystyrene on the water surface is assumed to be a continuous film with the bulk density 1 g/cm^3, the apparent thickness of the films, d_{app}, can be calculated from A_0; d_{app} is, of course, different from the thicknesses of the monomolecular particles. The lower figure of Figure 8 shows the apparent thickness d_{app} and the square root of the limiting area, $(A_0)^{0.5}$. For convenience if a molecule on the water is assumed to be a square prism, this value corresponds to the two sides, as indicated in Figure 8.

The apparent thickness, d_{app}, is almost constant, 40 Å, at molecular weights more than 4000. Below the molecular weight 4000, with decreasing the molecular weight d_{app} increased considerably and reached 490 Å at the molecular weight 1050. On the other hand, $(A_0)^{0.5}$ was about 900 Å at the molecular weight 2.06 × 10^6 and simply decreased with decreasing the molecular weight to 4000. Below the molecular weight 4000, with decreasing the molecular weight d_{app} increased considerably and reached 490 Å at the molecular weight 1050. At the higher molecular weight regime ($M_w > 3.84 \times 10^6$), $(A_0)^{0.5}$ was more than 10 times larger than the thickness d_{app}, thus the molecules exist in

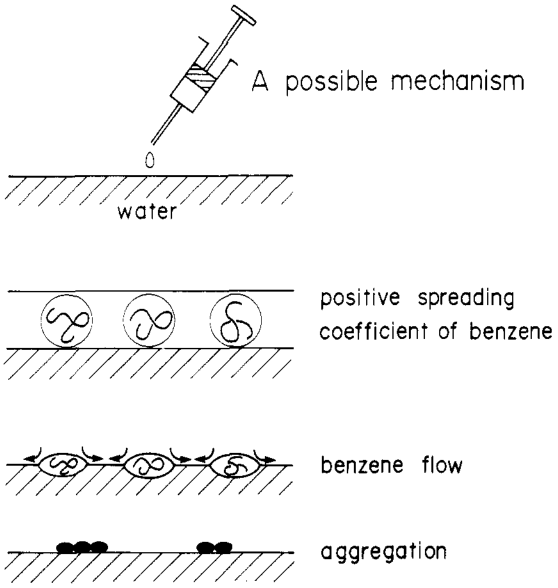

Figure 9. Schematic representation of a possible mechanism for the formation of the monomolecular particles.

flat shapes; this result agrees qualitatively with the TEM observation of the monomolecular particles.[9] In contrast, at the lower molecular weight regime ($M_w < 50\,000$), $(A_0)^{0.5}$ became smaller than d_{app}, thus the particles seem to stand on the water surface; this is unreasonable, thus it seems that the monomolecular particles are not formed at this lower molecular weight regime or the particles are stacked at the area A_0. Due to the limiting resolution of TEM, formation of monomolecular particle was not confirmed. This point is reserved for further studies.

6. A Possible Mechanism of the Formation of the Monomolecular Particles. The mechanism may be considered to follow the route indicated in Figure 9. Polystyrene, itself, does not have sufficient affinity to be able to spread on the water surface because of the lack of hydrophilic groups, but benzene spreads due to the positive spreading coefficient, thus polystyrene dilute solutions in benzene spread on the water surface. As a result of the spreading the polystyrene molecules are pulled apart from each other. With evaporation the concentration increases; as benzene is a good solvent for polystyrene, polystyrene does not precipitate from the solution during the evaporation. After further evaporation, the solution should become small droplets of relatively concentrated solution, each of which contains one polystyrene molecule. The reason why these small droplets do not aggregate with each other seems to be (1) because the droplets are so apart from each other that during the evaporation the droplets cannot contact or (2) because the flow of benzene from these droplets due to its positive spreading coefficient protects the contact of the droplets. After almost all benzene is evaporated, the monomolecular particles on the water surface aggregate by the Brownian motion as shown in Figures 2a and 3c.

IV. Summary

The behavior of a monolayer of polystyrene monomolecular particles was studied by the π–A curves and TEM. The surface pressure observed by this study was mainly mechanical force due to the compression. But in the high molecular weight regime, where the formation of the monomolecular particles was confirmed by TEM, results of the macroscopic observation (π–A curves) were consistent with the microscopic observation by TEM, indicating although polystyrene has no hydrophilic groups, the particles are stable on the water surface against the compression. In contrast, in the lower molecular weight regime ($M_w < 50\,000$), the apparent thickness, d_{app} became larger than $A_0^{0.5}$, indicating the monomolecular particles were not formed on the water surface or were unstable against the compression. Due to the limiting reslution of TEM, formation of monomolecular particles in this molecular weight regime was not confirmed. This point is reserved for further studies.

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References and Notes

(1) As polystyrene has no hydrophilic group, the surface pressure measured by the film balance is not due to the real decrease of the surface tension but a mechanical force necessary for rearrangement of the particles; thus the surface pressure discussed in this article is apparent surface pressure. This will be discussed in section III-3.
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