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Polystyrene Monomolecular Particles Obtained by Spreading Dilute Solutions on the Water Surface

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ABSTRACT: Ultrafine particles, each containing a single polystyrene molecule (monomolecular particles), were obtained by spreading very dilute (about 2×10^{-6} g/mL) solutions of polystyrene in benzene drop-by-drop onto a water surface. The molecular weights of the polystyrenes were from 3.84×10^6 to 8.42×10^6, each sample having a polydispersity (M_w/M_n) less than 1.17. The particles were observed by transmission electron microscopy. From the five points below, they were concluded to be monomolecular particles: (1) reasonable concentration dependence of diameter distributions, (2) clear molecular weight dependence of diameter distributions, (3) good empirical fit of observed diameter distributions to those calculated from molecular weight distribution data, (4) bimodal diameter distribution of particles obtained from a polymer sample having a bimodal molecular weight distribution, and (5) reasonable thicknesses of the particles as measured by shadowing with Pt-C.

I. Introduction

According to polymer solution theory, it is well-known that in dilute solution polymer chains exist as single molecules.[1] Therefore if solvent can be removed from this state with the polymer chains remaining isolated from each other, in principle it is possible to obtain particles which consist of a single polymer molecule.

For convenience these particles will be called "monomolecular particles". In the case of low molecular weight compounds, a monomolecular particle corresponds to one gas-state molecule. Therefore this term has no meaning. But in the case of polymers, the monomolecular particle is considered to have particle properties. By simple calculation, the monomolecular particle of a polymer that has a molecular weight of several million is expected to have a diameter of a few hundred angstroms. Therefore it is meaningful to call this molecule a "monomolecular particle".

Monomolecular particles are considered to have interesting properties from two standpoints. The first is that they consist of one molecule. Thus they are free from the intermolecular entanglements that are essential for ordinary polymer solids. The second is the small diameters of particles, which are not easily obtained by other methods. These particles have a large surface area, thus they are expected to be suitable materials for the study of surface properties of polymers.

But obtaining monomolecular particles is very difficult because usually removal of solvent from the solution causes an increase in concentration and ultimately it causes entanglement of polymer chains. Therefore special techniques are required. Previous workers reported that monomolecular particles of synthetic polymers were obtained by spraying dilute solutions onto substrates.[2-5] These works are very interesting in that they provide the evidence for monomolecular particles. This spray method will be discussed in comparison with a new method.

In the present work, a new method was developed to obtain monomolecular particles of polymers. They were obtained by spreading dilute polystyrene solution in benzene on a water surface. The obtained particles were concluded to be monomolecular by detailed examination of particle diameter distributions by transmission electron microscopy.

II. Experimental Section

Commercially available high molecular weight polystyrenes of narrow molecular weight distributions were used (Toyo Soda Mfg. Co., Ltd., Japan). Characterization data of the polymers are summarized in Table I with sample codes and the overlapping concentration C^*. C^* is defined by $C^* = 3M/(4\pi\langle s^2\rangle^{3/2}N_A)$, where M is the molecular weight of the polymer, $\langle s^2\rangle$ is the mean-square radius of gyration, and N_A is Avogadro's number. Below this concentration C^*, polymers exist as single chains in solution. In a typical experiment, the concentration of the solution that was spread on the water surface was about 2×10^{-6} g/mL, which is at least less than $^1/_{400}$ of C^*. Therefore, the polymer in the solution exists as single molecules.

Reagent grade benzene was used after distillation. Water was distilled twice from a quartz still. Glass apparatus was etched by concentrated KOH-ethanol solution and thoroughly rinsed with doubly distilled water. A commercial Langmuir-type film balance[6] (LAUDA Film Balance) was used as a trough. It consists of a Teflon-coated trough, a Langmuir-type surface pressure measuring unit, and a moving barrier. It measures the surface pressure (difference of the surface tensions between pure surface and covered surface) as a function of the area A occupied by the molecules.

Ultrafine particles of polystyrene were obtained as described below. A drop of dilute polystyrene 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, ultrafine particles were obtained on the water surface. Temperature of the water was 20 °C. Typically 2 mL of the solution was spread on a water surface of 562 cm^2; the surface was compressed by moving the barrier to 56.2 cm^2 at a rate of 15 cm^2/min.

The relation between surface pressure π and area A of these particles on the water surface was investigated prior to this work.[7] It showed compression film type π-A curves, which are the same as those reported previously.[8,9] The zero extrapolated area A_0, which is defined by extrapolating the maximum slope of π-A curve to zero surface pressure, was $2.6 \pm 0.4 \times 10^3$ cm^2/mg, being almost independent of the molecular weight of polystyrenes used in this study. The compressed area used for obtaining TEM samples (1.4×10^4 cm^2/mg) was therefore about five times larger than A_0.

After compression, the particles were transferred to transmission electron microscope copper grids, which were covered with collodion film reinforced with evaporated carbon, by touching the grid surface to the water surface. These were observed by TEM without further treatment such as staining. Particle diameter distributions were obtained manually by measuring 120-240 particles in the TEM pictures by use of an ordinary ruler. The magnifications of the pictures were about 100000×, thus the accuracy of this manual measurement, ±0.1 mm, corresponded to ±10 Å in the measured diameters.

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Table I
Characterization of Polystyrenes Determined by GPC and Light Scattering Compared with Those Calculated from Particle Diameters

	$M_w \times 10^{-6}$		$M_n \times 10^{-6}$		M_w/M_n			
sample code	LS[a]	TEM[b]	c	TEM[b]	GPC[d]	TEM[b]	$\langle s^2\rangle^e \times 10^{10}$, cm^2	$C^* \times 10^3$, g/mL
F-380	3.84	3.8	3.69	3.4	1.04	1.1	0.991	1.54
F-450	4.48	4.4	3.93	3.9	1.14	1.1		
F-550	5.48	5.1	4.77	4.6	1.15	1.1	1.41	1.30
F-700	6.77	6.8	5.94	6.4	1.14	1.1	1.83	1.08
F-850	8.42	8.4	7.20	7.8	1.17	1.1	2.47	0.86

[a] Measured by light scattering; see note 10. [b] Calculated from the diameter distributions with eq 1. [c] Calculated from *a* and *d*. [d] Measured by GPC; see note 11. [e] Measured by light scattering; see note 10.

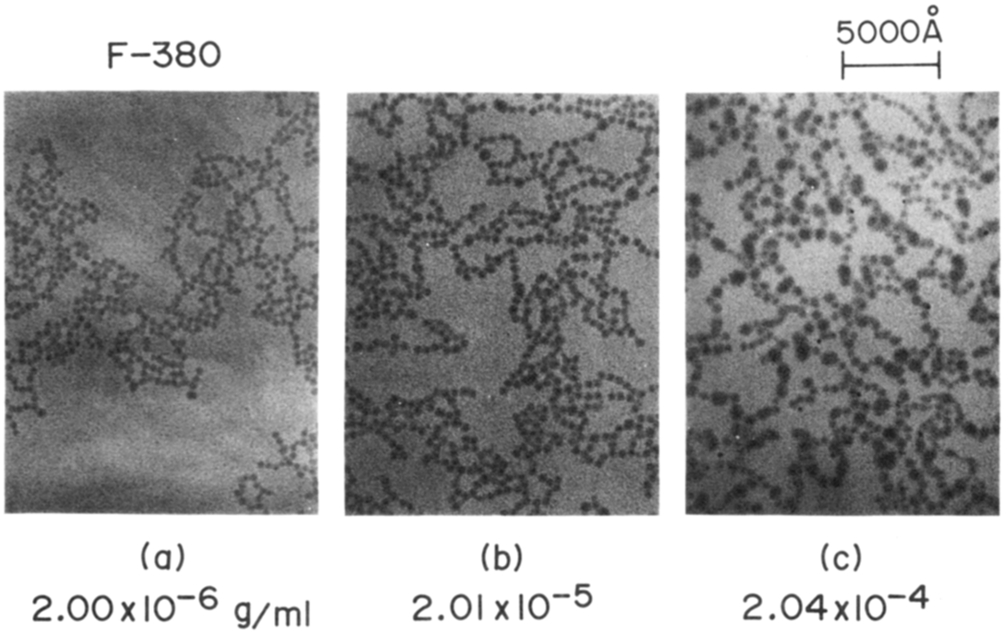


Figure 1. Transmission electron micrographs of ultrafine particles of F-380 obtained from various concentration solutions. The ratios of the concentration C to the overlapping concentration C^*, C/C^*, are (a) 1/770, (b) 1/77, and (c) 1/7.5.

Shadowing was used to measure the thicknesses of the particles. Particles on a water surface were transferred onto mica in the manner mentioned above. An emulsion of polystyrene latex, the diameter of which is 0.109 μm, was sprayed on the same mica as the standard for determining the shadowing angle. The samples were shadowed through a 1.4-mm slit with platinum–carbon simultaneous shadowing. After further evaporation of carbon onto them, the resultant film on the mica was floated off onto water, transferred onto copper grids, and then observed by TEM.

III. Results and Discussion

1. Concentration Dependence of Particle Diameter Distribution. Figure 1 shows transmission electron micrographs of ultrafine particles of F-380 obtained from various concentration solutions. The solution concentrations C were (a) 2.00×10^{-6}, (b) 2.01×10^{-5}, and (c) 2.04×10^{-4} g/mL, and the ratios of C to overlapping concentration C^*, C/C^*, were (a) 1/770, (b) 1/77, (c) 1/7.5, respectively. Black nodules in the micrographs represent polystyrene particles on the collodion film.

An inspection of the micrographs indicates that with decreasing concentration of the original solution the larger particles disappear and the diameter distribution becomes sharper. It is noted that particles obtained from the 2.04 $\times 10^{-4}$ g/mL solution already contain particles of the same size as were obtained from the 2.00×10^{-6} g/mL solution, but the number of them was small.

When the 2.04×10^{-4} g/mL solution was spread, a small amount of floating material was visible. It was considered to be macroscopically aggregated polystyrene. By TEM, in almost all areas a stringlike structure was observed among the particle structure. This structure is considered to be highly connected ultrafine particles, but in a few areas, only the particle structure was observed, as shown in Figure 1c.

In the case of the 2.01×10^{-5} and 2.00×10^{-6} g/mL solutions, there was no floating material visible on the water surface after the solutions were spread. By TEM ultrafine particle structures were observed in all areas. However, even in the case of 2.00×10^{-6} g/mL solution, in some areas extraordinarily large particles were observed among the smaller particles, but the number of the larger ones was considerably smaller, less than 1 in 100. Therefore in this study, the areas containing extraordinarily large particles were ignored.

Figure 2 shows the diameter distributions of particles corresponding to the micrographs in Figure 1. The diameter distributions were measured manually from the transmission electron micrographs, the magnifications of which were about 100000×, as described above.

In order to obtain precise diameters, precise boundaries of the particles must be determined. But, usually it is difficult to determine precise boundaries, because particles in TEM pictures usually have vague boundaries. The particles in this work also had vague boundaries. But the particles obtained on the water surface were in contact with each other, thus it was possible to determine the boundaries more precisely from the contact points of the particles. In this work the contact point, therefore the

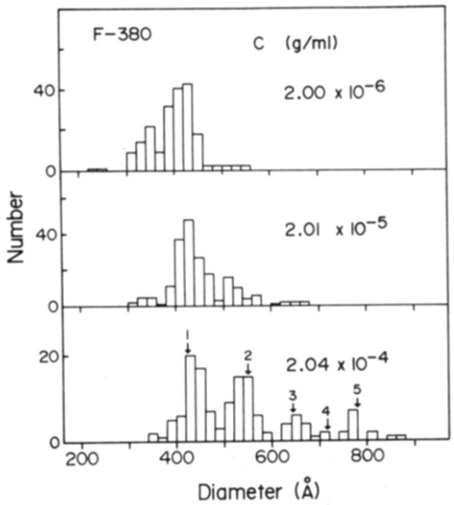


Figure 2. Particle diameter distributions of ultrafine particles of F-380 obtained from various concentration solutions. The five arrows in the figure indicate expected peak positions for particles that contain one to five molecules, respectively; the peak positions were calculated with empirical eq 1.

boundary of the particle, was defined to be the point of minimum contrast between an adjacent pair of particles. By this definition, the diameters were determined more precisely. This connected structure was formed probably because of attractive interaction between particles after they were produced on the water surface.

The diameters of the particles obtained from the 2.04 $\times 10^{-4}$ g/mL solution have a broad distribution with at least two significant peaks at diameters about 420 and 540 Å. With decreasing concentration, particles of larger diameter disappeared and only smaller particles, the diameter distribution of which peaked sharply at about 420 Å, were observed. These facts indicate that these small particles have a limiting size and cannot be divided into smaller parts. That is, they are monomolecular particles.

The five numbered arrows in Figure 2 indicate the expected peak positions of the diameter distributions for ultrafine particles that contain one to five molecules, respectively. These peak positions were calculated from the empirical eq 1, which was derived from the relation between molecular weight and particle diameter, as will be discussed in section III-2. As shown in this figure, if the molecular weight distribution of the original polymer is sharp enough, particles that contain only a few molecules are expected to have a discrete diameter distribution. The two peaks at about 420 and 540 Å agree with the expected peaks for particles that contain one and two molecules, respectively.

On the basis of this data, subsequent experiments were carried out with solutions containing about 2×10^{-6} g/mL polystyrene.

2. Molecular Weight Dependence of Particle Diameter Distributions. Figure 3 shows transmission electron micrographs of particles obtained from polystyrenes having weight-average molecular weights 3.84×10^6 (F-380), 4.48×10^6 (F-450), 5.48×10^6 (F-550), 6.77×10^6 (F-700), and 8.42×10^6 (F-850). Close inspection of the pictures indicates that each photograph shows particles of narrow diameter distribution and that with increasing

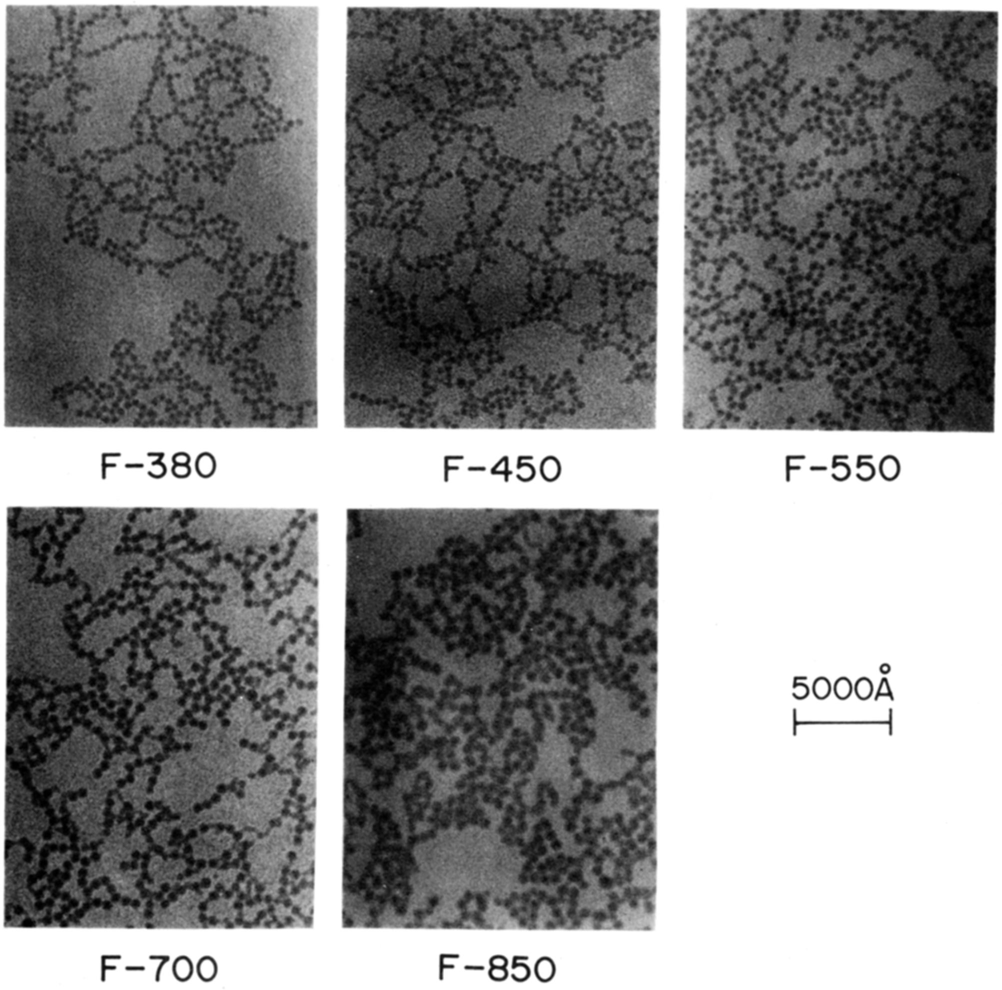


Figure 3. Transmission electron micrographs of monomolecular particles obtained from various molecular weight polystyrenes.

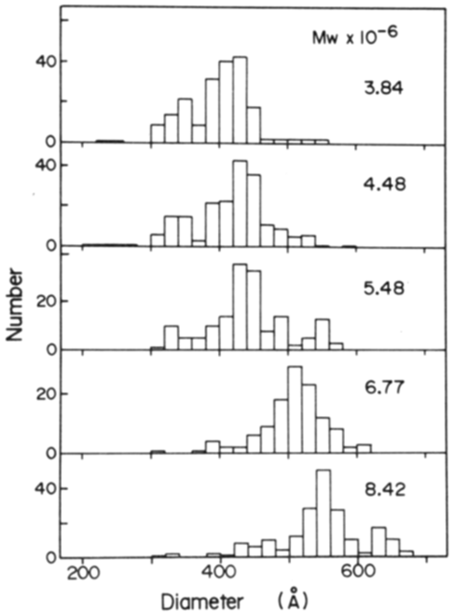


Figure 4. Particle diameter distributions of monomolecular particles obtained from various molecular weight polystyrenes.

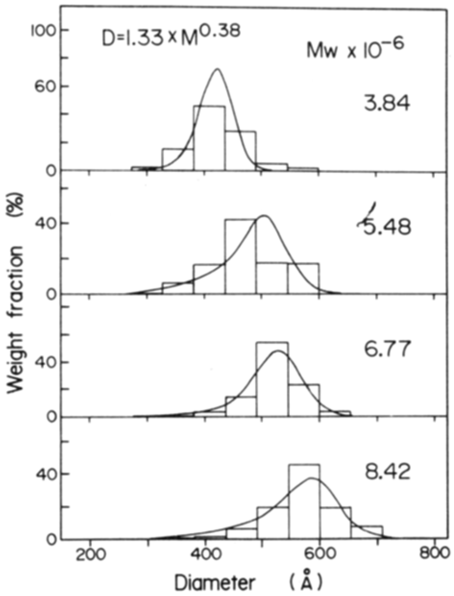


Figure 5. (Histograms) Diameter distributions observed by TEM. (Solid lines) Diameter distributions calculated from GPC molecular weight distribution data by means of eq 1.

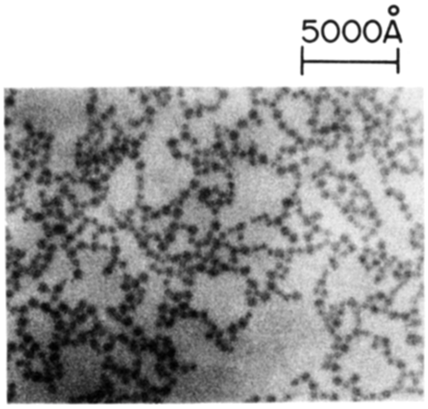


Figure 6. Transmission electron micrographs of monomolecular particles obtained from an equimolar mixture of F-380 and F-850.

molecular weight the diameters of the particles increased.

Figure 4 shows the particle diameter distributions for the particles corresponding to the micrographs in Figure 3. Each micrograph shows a sharp diameter distribution, and a clear correlation between particle diameter and the molecular weight of the original polymer is apparent. The number-average diameters are 400 (F-380), 417 (F-450), 444 (F-550), 508 (F-700), and 545 Å (F-850), respectively. These results strongly indicate that each particle contains one molecule.

The relation between peak diameters and molecular weights in Figure 4 is given by the empirical equation

$$D = 1.33 \times M^{0.38} \tag{1}$$

where D is the diameter of a particle in angstroms and M is the molecular weight of the polymer. With this equation we can estimate the molecular weight of each particle shown in the transmission electron micrographs.

3. Comparison between Particle Diameter Distributions and Molecular Weight Distributions. If these particles are monomolecular particles, the diameter distributions in Figure 4 should correspond to the molecular weight distributions of the original polystyrenes. By means of the empirical eq 1, diameter distributions were calculated from the molecular weight distribution data. Figure 5 shows the calculated diameter distributions (solid lines) along with the observed diameter distributions (histogram). The molecular weight distributions were measured by gel permeation chromatography.[11] The vertical axis corresponds to weight fraction. Therefore, the observed diameter distributions were corrected to represent weight fraction by multiplying the number of particles by the molecular weight calculated with eq 1. A good fit is apparent between the calculated distributions and those observed.

The weight-average molecular weight M_w, the number-average molecular weight M_n, and the polydispersity index M_w/M_n were also calculated from the diameter distributions in the same way. They are summarized in Table I. The calculated values are in sufficient agreement with the characterization data.

4. Ultrafine Particles from a Polymer Sample Having a Bimodal Molecular Weight Distribution. If the particles are monomolecular, then those obtained from a polymer sample having a bimodal molecular weight distribution must also have a bimodal diameter distribution. Figure 6 shows a transmission electron micrograph of particles obtained by spreading an equimolar mixture solution of F-380 and F-850 in benzene in the same manner as described above. Figure 7 shows the diameter distribution of particles from the mixture along with those of the component polymers. The particles from the mixed solution have a clear bimodal diameter distribution, each peak corresponding to one of the original polymers. The small inside shift of the two peaks is thought to be because of overlap of the two peaks. The ratio of the number of particles under the small-diameter peak to that for the large-diameter peak is about 0.97 ± 0.03 and is almost identical with the original mixing ratio. These facts strongly imply that these are monomolecular particles.

5. Thickness of Ultrafine Particles. The diameters of the ultrafine particles obtained by this method are much larger than those estimated by assuming that a monomolecular particle is a perfect sphere of density equal to that of bulk polystyrene (1 g/cm^3). For example, in the case of F-700, the former diameter is 508 Å, whereas the latter is 278 Å. If the particles obtained by this method have almost the same density as bulk polystyrene, their thicknesses must be much smaller than their diameters. In order to confirm this point, the thickness of the particles

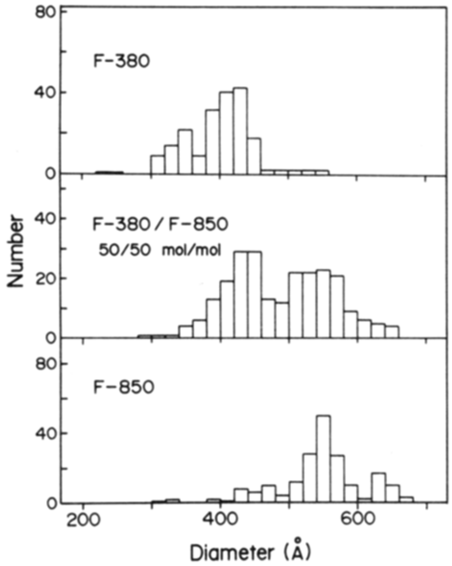


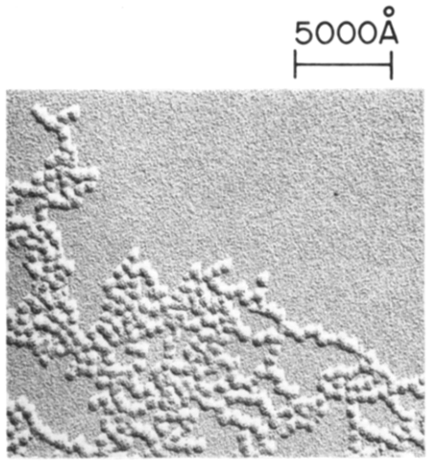
Figure 7. Diameter distribution of monomolecular particles obtained from an equimolar mixture solution of F-380 and F-850 along with diameter distributions of the original polymers.

was measured by shadowing.

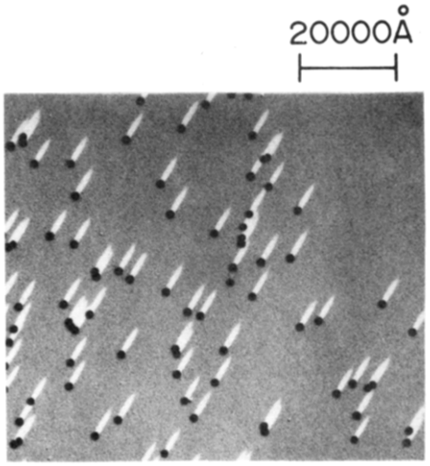
Figure 8 shows the transmission electron micrographs of shadowed (a) ultrafine particles of F-700 and (b) polystyrene latex particles of diameter 0.109 μm. They were both mounted on a single flake of mica and shadowed through a 1.4-mm slit with platinum–carbon. The shadow angle was estimated to be 13° from the shadow length of the polystyrene latex particles. An inspection of the micrographs indicates that the shadows of spherical polystyrene latex particles are several times longer than the diameter, whereas the shadows of F-700 are almost the same as the diameter. This confirms that the ultrafine particles obtained by this method are very flat. There are several difficulties in determining exact thickness by shadowing. The first problem is contamination, which may cover the particles. The second is the thickness of the evaporated metal, which evaporates not only onto the substrate but also onto the particles themselves. From the amount of metal consumed in this experiment, the thickness of the evaporated metal was estimated to be some 10 Å. This assumes that only platinum had been evaporated. However, in practice, carbon was also evaporated with the platinum. Thus the thickness was more than 10 Å. The thicknesses below are thus overestimated somewhat. These problems aside, the thickness of F-700 ultrafine particles was estimated to be about 100 Å. In contrast, we calculated the thickness of this particle to be 84 Å by assuming that this particle is a flat spheroid with major axis 508 Å and density equal to that of bulk polystyrene (1 g/cm^3). Taking the above problems into consideration, we can conclude that both observed and calculated values are almost the same. But further quantitative studies will be required to determine the exact shape of particles and the precise value of the density.

6. Comparison with Spray Method. As mentioned in the Introduction, there are reports about monomolecular particles of synthetic polymers obtained by the spray method.[2-5] The object of these works was to obtain molecular weights and molecular weight distributions of polymers by direct observation of single molecules using transmission electron microscopy.

Siegel and co-workers reported a very interesting result.[2] They obtained ultrafine particles of polystyrene by spraying dilute polystyrene solutions in cyclohexane onto collodion substrates. these were then observed by TEM after shadowing with uranium. They reported that the molecular weights calculated from the volume distribution of particles by assuming that the density of the particles is the same as in the bulk are almost the same as the molecular weights measured by osmotic pressure and intrinsic viscosity for four different molecular weight samples.



(a) F-700



(b) Polystyrene latex

Figure 8. Transmission electron micrographs of (a) monomolecular particles of F-700 and (b) polystyrene latex particles of diameter 1.09 μm. Both were on one mica plate and shadowed with platinum–carbon at an angle of 13°.

On the other hand Richardson reported that he could not reproduce Siegal's results.[3] He developed a mixed-solvent spray method to get reproducible results. He dissolved polymers in mixed solvents which consisted of a volatile good solvent and a relatively less volatile poor solvent for polymers. In the starting solution, the polymer chains are dissolved without entanglements. After the solutions are sprayed on the substrate and as the solvent evaporates, the ratio of the poor solvent to the good solvent increases. As a result, the polymer chains become tightly coiled and then become monomolecular particles. He also identified the resultant particles as being monomolecular by comparing observed particle dimensions with those calculated from molecular weight assuming bulk density. Similar results were reported by other workers.[4,5]

These reports show the existence of monomolecular particles. But by this spray method, in principle, only the small number of particles can be obtained per unit area. If much solution is sprayed on the substrate to obtain many particles, entanglement of the molecules will occur with evaporation of the solvent and thus monomolecular particles cannot be obtained. This small number of particles in the spray method highly restricts observations other than TEM. On the other hand, in a recent work, particles obtained on a water surface were collected to cover about 60% of the water surface by moving the compressing barrier and accumulated on a substrate by touching it to the water surface repeatedly.[12] Thus the number of particles obtained per unit area of the substrate is much larger than that in spray method. Thus this method is suitable not only for TEM observation but also for measuring other physical and chemical properties of particles. As mentioned in the Introduction, monomolecular particles are considered to have interesting properties from two standpoints. The first is that they consist of one molecule. Therefore, they are free from intermolecular entanglements, which are essential for polymer solids. This is an extraordinary state, thus the properties are interesting. The second is the small diameter of the particles, which is not easily obtained by other methods. (By decreasing the molecular weight of the polymer, it may be possible to obtain smaller particles than those studied in this paper. However, this was not tried because of the limited resolution of TEM.) With decreasing diameter, the surface area per unit volume becomes larger. Thus the surface properties will become dominant and detectable. Therefore, these particles are considered to be suitable materials to study surface properties of polymers.

IV. Conclusions

The ultrafine particles obtained by spreading dilute polystyrene solutions in benzene on a water surface are monomolecular particles because (1) with decreasing concentration of starting polymer solution, the diameter distribution of obtained particles became sharper and converged to limiting value; (2) a dependence of diameter on molecular weight was clearly observed; (3) a good fit was obtained between observed diameter distributions and those calculated from molecular weight distribution data measured by GPC; (4) particles from the mixed solution containing polystyrenes of two different molecular weights had a bimodal diameter distribution, each peak corresponding to a diameter distribution of a component polystyrene; and (5) the measured thickness of the particles was consistent with the value calculated by assuming bulk density.

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Registry No. Polystyrene, 9003-53-6.

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(10) From the data sheet of Toyo Soda. Measurements were conducted in benzene at 30 °C by means of a low-angle light-scattering photometer. The incident beam was vertically polarized light with a wavelength of 436 nm. $dn/dc = 0.113$ mL/g. The weight-averaged molecular weight M_w and the radius of gyration $\langle s^2 \rangle$ were then evaluated by using Berry's square-root plots.
(11) From the data sheet of Toyo Soda. Measurements were made in tetrahydrofuran at 25 °C on a Toyo Soda HLC-802UR GPC apparatus. A UV spectrometer was operated as a concentration detector, and four TSK-GEL G6000H6 columns were used, each of which was 60 cm in length and 7.5 mm in inner diameter, packed with polystyrene gel particles with a porosity of 10^6 Å. The number of theoretical plates was more than 6000 plates/ft. The injection was 0.5 mL, and sample concentration was 0.2 mg/mL. Flow rate was 1.0 mL/min.
(12) Kumaki, J., to be submitted for publication.

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pH-Induced Regulation of the Permeability of a Polymer Membrane with a Transmembrane Pathway Prepared from a Synthetic Polypeptide

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ABSTRACT: A novel polymer membrane having a transmembrane permeating pathway ("channel") was prepared from a synthetic polypeptide by using the newly synthesized poly(butyl methacrylate)–polypeptide graft copolymer as the material. The transmembrane continuous phases of the hydrophilic polypeptide were suggested to be formed in the stable matrix from vinyl polymer and to function as a permeating pathway for polar substances. The infrared spectra of the membrane showed the pH-dependent conformational change of the polypeptide segment. Regulation of the permeability was performed by pH based on the conformational change of polypeptide composing the pathway.

Introduction

Membrane proteins, distributed like a mosaic in the phospholipid bilayer, play important roles in the life process, including the transport of substances, metabolism, and the transmission of information. Some of the membrane proteins are considered to form a "hole" or a "channel" for transporting a specific substrate across the membrane and control the permeability by conformational change corresponding to external stimuli.

Numerous model systems from polymer membranes have been reported, which mimic the function of biomembrane. As for the specific, facilitated, and/or active transport, cation- or anion-exchange polymers,[1] a crown ether containing polymer,[2] a polymer carrying lactone derivatives,[3] and polymers incorporating moieties that undergo reversible isomerization, such as the *N*-hydroxy-

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