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Aggregation Structure of a Two-Dimensional Ultrathin Polystyrene Film Prepared by the Water Casting Method

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ABSTRACT: A two-dimensional ultrathin film was defined as a film with a dimension thinner than that of an unperturbed chain. The aggregation structure of the two-dimensional ultrathin polystyrene (PS) film prepared by the water casting method was examined. The radius of gyration of a PS chain in the two-dimensional ultrathin film was evaluated from small angle X-ray scattering (SAXS) and small angle neutron scattering (SANS) measurements. The radius of gyration along the direction parallel to the film surface was found to be larger than the radius of gyration of an unperturbed chain. The apparent occupied volume for a corresponding chain, which consists of overlapping of a noticed chain and surrounding chains, was calculated from the radius of gyration and film thickness. The apparent volume in the two-dimensional ultrathin film was found to be smaller than that in the three-dimensional solid film, indicating that the amount of interpenetration of surrounding chains is small; that is, the degree of entanglement among chains is low. A PS chain with a low degree of entanglement in the two-dimensional ultrathin film was expanded along the direction parallel to the film surface owing to unequilibrium characteristics of the film formation process. The radial distribution function (RDF) in the two-dimensional ultrathin film was also obtained from the Fourier transform of the wide angle X-ray scattering profile. The shape of the peak corresponding to intermolecular distance in the two-dimensional ultrathin film was broadened toward the long distance side, indicating that the packing of PS chains in the two-dimensional ultrathin film was looser than that in the three-dimensional solid film.

Introduction

In order to use ultrathin polymer films in special functions, it is important to understand the aggregation state of polymer chains in these ultrathin films. A flexible polymer chain in a three-dimensional amorphous bulk state behaves as an unperturbed chain.[1] In comparison, it is very important and interesting to study the aggregation stucture of a polymer chain for the case when the film thickness is smaller than the dimension of an unperturbed chain. Polymer chains in such a system are restricted in a small spatial dimension perpendicular to the film surface and then the conformational entropy of an individual chain may become smaller than that in a three-dimensional solid state. Therefore, it is reasonable to expect that the aggregation structure and mechanical properties of such ultrathin films are different from those of the three-dimensional amorphous solid film.

The conformation of an isolated polymer chain in the two-dimensional state has been investigated theoretically and numerically, in which a polymer chain is confined between two plates.[2–6] In the case of an unperturbed Gaussian chain without excluded volume, the segment density distribution along one direction (e.g. parallel to the plate) is independent of that along the other direction (e.g. perpendicular to the plate). This implies that the segment density distribution along the direction parallel to the plate does not change, even if the segment density distribution of a chain along the direction perpendicular to the plate is restricted to a small spatial dimension. Thus, the radius of gyration of an unperturbed chain along the direction parallel to the plate should be equal to that of an unperturbed chain in the three-dimensional state. On the contrary, in the case that a perturbed chain with excluded volume is restricted in small spatial dimension along the direction perpendicular to the plate, the excluded volume affecting the segment density distribution along the direction parallel to the plate is augmented by that along the direction perpendicular to the plate. Therefore, the perturbed chain dimension along the direction parallel to the plate becomes larger than the perturbed chain dimension in the three-dimensional state.

Some experimental results about the conformation of isolated polymer chains in the two-dimensional state have been reported.[7–10] The mass of polymer per unit surface area was regarded as the concentration of the two-dimensional solution state, and also, the relation between the surface pressure and concentration was discussed on the basis of scaling theory. Under an apparent θ condition of two-dimensional solution state, the dimension of a polymer chain was reported to be proportional to the one-half power of the molecular weight and also, apparent excluded volume effect depended on the temperature and polymer flexibility. In contrast, the conformation of polymer chains in the two-dimensional polymer solid state, where the polymer chains aggregated and entangled, has not been investigated.

The formation process of the morphologically homogeneous ultrathin film by the water casting method has been discussed.[11] In this process, the solution spread on the water surface depending on the dissipation speed of solvent into both air and water, and finally the almost dried thin film was formed on the water surface. The entanglement among polymer chains plays an important role in maintaining the integrity of the film. That is, entanglements act as joints among chains to prevent the formation of isolated particles during spreading of solution on the water surface. Since the thickness of ultrathin films (around 20 nm) was smaller than the dimension of an unperturbed chain, the ultrathin film which was prepared

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by the water casting method was considered to be a two-dimensional ultrathin film.

The purpose of this study is to investigate the aggregation structure of the two-dimensional ultrathin PS film prepared by the water casting method. The conformation of a PS chain in the two-dimensional ultrathin film was investigated by small angle X-ray scattering (SAXS) and small angle neutron scattering (SANS) measurements. The aggregation state of PS chains in the two-dimensional ultrathin film was also discussed on the basis of the radial distribution function (RDF) which was obtained from the wide angle X-ray scattering profiles.

Experimental Section[29]

Sample Preparation. Samples used for the preparation of two-dimensional ultrathin films were all commercially available monodisperse polystyrenes with the weight-average molecular weight, M_w, of 190 000 (Tosoh Co. Ltd.), 233 000 (Pressure Chem. Co. Ltd.), and 520 000, 1 030 000, 1 450 000, and 6 390 000 (Polymer Lab. Co.) and M_w/M_n, where M_n was a number-average molecular weight, of 1.04, 1.06, 1.05, 1.05, 1.06, and 1.12, respectively. For SANS measurements, deuterated PS (D-PS) with M_w of 185 000, 530 000, and 1 000 000 (Polymer Lab. Co.), and M_w/M_n of 1.02, 1.09, and 1.18, respectively, were used. The two-dimensional ultrathin film was prepared by the water casting method by carefully spreading a single droplet of polymer solution on the water surface.[11] Cyclohexanone solutions of 0.5–2.0 wt % were used and spread on the water surface at 293 K.

Evaluation of the Radius of Gyration of a Chain in Two-Dimensional Ultrathin Film. The radius of gyration of a polymer chain in the two-dimensional ultrathin film was evaluated by SAXS measurements on the basis of the tagged-polymer method.[12] The conformation of a tagged-PS chain in the matrix of regular PS chains can be evaluated from the analysis of the excess scattering due to the tagged-atom with high scattering power. As the tagged-PS, a random copolymer composed of styrene and *p*-iodostyrene was prepared by partial iodination of PS[13] with M_w of 1 450 000. The mole fraction of *p*-iodostyrene monomer in the copolymer was 15.7%. The sample for SAXS measurements was prepared by 100 times stacking of 1000-layered ultrathin films which were picked up 1000 times from the water surface. On the other hand, the three dimensional solid film was prepared from a cyclohexanone solution by solvent casting method and then, annealed above the glass transition temperature. The three-dimensional solid film can be considered to be a bulk sample in its equilibrium state. The samples of regular PS together with 1.5 mol % of tagged-PS were prepared. The scattered intensity was measured with a SAXS diffractometer (Rigaku, CN2203E3) fitted with a Kratky U-slit. A stabilized generator (Rigaku, Rota-Flex RU-200) operating at 50 kV and 200 mA was used as Cu Kα X-ray source. The measured *q* range for SAXS analysis was 1.5×10^{-4} to 1×10^{-3} nm. The error from slit length was corrected by Schmidt's method.[14] The excess scattering was plotted according to Guinier's procedure[15]

$$I(\mathbf{q}) = I(0)\exp(-{}^{1}/_{3}\mathbf{q}^{2}\cdot\langle S^{2}\rangle) \tag{1}$$

$$\mathbf{q} = \frac{4\pi\sin\theta}{\lambda}$$

where $\mathbf{q}$ and $\langle S^2\rangle$ are the scattering vector and the mean square of the radius of gyration, respectively. $I(\mathbf{q})$ and $I(0)$ are the excess scattered intensities at $\mathbf{q}$ and $\mathbf{q} = 0$, respectively. From the initial slope of the plot of ln $I(\mathbf{q})$ vs $\mathbf{q}^2$, the radius of gyration, $\langle S^2\rangle^{1/2}$ of the tagged-PS was evaluated.

In order to evaluate the radius of gyration of a polymer chain in the two-dimensional ultrathin film by SANS measurements, a mixture of 20 vol % of D-PS and 80 vol % of PS was used. The samples for SANS measurements were prepared by 30 times stacking of 2000-layered ultrathin films. Since the Flory χ parameter between D-PS and PS is almost zero,[16] the radius of gyration of a PS chain can be evaluated by fitting the Debye function to the excess scattering of the mixture after subtraction of the incoherent background from PS. The Debye function, $S_{\mathrm{Debye}}(\mathbf{u})$ is given by eq 2.

Table I. Thickness, *t*, and Two-Dimensionality, *D*, of a Two-Dimensional Ultrathin Film and Radius of Gyration in a Three-Dimensional Solid Film, $\langle S^2\rangle^{1/2}_{3D}$, and Radius of Gyration in a Two-Dimensional Ultrathin Film, $\langle S^2\rangle^{1/2}_{2D\text{-}II}$

method	M_w	*t* (nm)	*D*	$\langle S^2\rangle^{1/2}_{3D}$ (nm)	$\langle S^2\rangle^{1/2}_{2D\text{-}II}$
SANS	190 000	19	0.77	12.3	15.0
	190 000	29	1.18	12.3	13.6
	520 000	19	0.49	18.4	27.8
	1 030 000	19	0.35	27.5	40.2
SAXS	1 450 000	14	0.21	34	52
	1 450 000	19	0.28	34	48
	1 450 000	29	0.43	34	42

$$S_{\mathrm{Debye}}(\mathbf{u}) = \frac{2}{\mathbf{u}^2}(e^{-u} + \mathbf{u} - 1) \tag{2}$$

$$\mathbf{u} = \mathbf{q}^2\cdot\langle S^2\rangle$$

SANS intensity was measured by 8-m SANS and 30-m SANS instruments at the National Institute of Standards and Technology (Gaithersburg, MD) with sample-detector distances of 3.6 and 12 m, respectively. The wavelength, λ, and $\Delta\lambda/\lambda$ were 1.2 nm and 0.2, respectively. The measured *q*-range for SANS analysis was 2×10^{-4} to 5×10^{-3} nm. Full width at half maximum of the scattering peak was 30 times larger than that of the incident neutron beam. Thus, the smearing effect was disregarded.

Estimation of RDF by Fourier Transform Analysis of Wide Angle X-ray Scattering. Samples for wide angle X-ray scattering measurements were prepared by 10 times stacking of 2000-layered ultrathin films. The wide angle X-ray scattering intensity was measured with a wide angle X-ray diffractometer (Rigaku, PMG-A2). A stabilized generator (Rigaku, Rota-Flex RU-300) operating at 50 kV and 300 mA was used as Cu Kα X-ray source.

The coherent scattering intensity, $I_{\mathrm{coh}}(\mathbf{q})$, is related to the radial distribution function, RDF, $P(r)$ as given by eq 3

$$P(\mathbf{r}) = 1 + \frac{1}{2\pi^2\mathbf{r}}\int_0^\infty \mathbf{q}\cdot i(\mathbf{q})\cdot\sin(\mathbf{q}\cdot\mathbf{r})\,\mathrm{d}\mathbf{q} \tag{3}$$

$$i(\mathbf{q}) = \frac{I_{\mathrm{coh}}(\mathbf{q})}{f^2} - 1$$

where $\mathbf{r}$ and f are the distance in a real space and the number average of scattering factor of atoms in PS, respectively. The experimentally obtained scattering intensity, $I_{\mathrm{ex}}(\mathbf{q})$, was corrected for polarization and absorbance and also was normalized by Krogh-Moe–Norman's method[17,18] in order to separate $I_{\mathrm{coh}}(\mathbf{q})$ from incoherent scattering intensity. The values of coherent and incoherent scattering factors were quoted from Cromer's[19] and Compton's[20] tables, respectively. The errors from truncation effect and noise in wide angle region were reduced by the modification function method.[21]

Results and Discussion

Conformation of a Polymer Chain in Two-Dimensional Ultrathin Film. Table I shows the results of the SANS and SAXS measurements. *t* is the thickness of the film which was evaluated by X-ray interference method.[11] *D* is the parameter of two-dimensionality, which will be explained later. $\langle S^2\rangle^{1/2}_{3D}$ and $\langle S^2\rangle^{1/2}_{2D\text{-}II}$ are the evaluated value of the radius of gyration in the three-dimensional solid film and that parallel to the film surface in the two-dimensional ultrathin film, respectively. Since X-ray and neutron beams were irradiated perpendicular to the film surface, the evaluated value of the radius of gyration, $\langle S^2\rangle^{1/2}_{2D\text{-}II}$ corresponds to that along the direction parallel to the film surface. Strictly speaking, the values of $\langle S^2\rangle^{1/2}_{3D}$ and $\langle S^2\rangle^{1/2}_{2D\text{-}II}$ evaluated by SAXS analyses are not the radius of gyration of a PS chain but that of a tagged-PS chain. According to Hamada et al.,[12] the exact value of the radius of gyration of a PS chain from SAXS

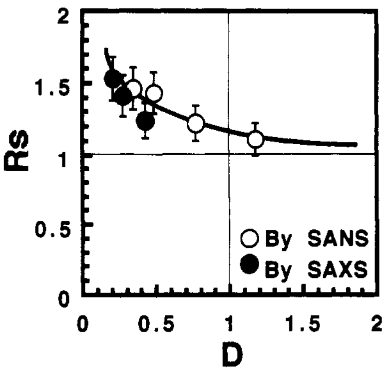

Figure 1. Relation between R_S and D. R_S is the ratio of radius of gyration of a chain in a two-dimensional ultrathin film parallel to the film surface to that in a three-dimensional solid film. D is the ratio of thickness to the end-to-end distance of unperturbed chain, and thus D means two-dimensionality.

measurements must be determined from an extrapolation to both zero iodine contents and zero fraction of tagged-PS. However, it is reasonable to assume that this comparison provides a relative measure of the radius of gyration in the two-dimensional ultrathin film with that in the three-dimensional solid film, because the conformation of a tagged-PS chain is similar to that of a regular PS chain.[12] There are another considerations that we must take into account. The q-range for SAXS analysis in this study was overpassed from Guinier criteria. Accordingly, the evaluated values of R_g from SAXS analysis were not so accurate and should have a tendency to be smaller than the accurate values. Also, SANS intensity should be measured at smaller q-ranges for evaluating the accurate R_g. For preparing two-dimensional ultrathin films, polystyrene with higher molecular weight than 1×10^5 was used. Therefore, the measured q-ranges were not so sufficient for evaluating the accurate R_g. However, it is reasonable to consider that the value of R_g in the two-dimensional ultrathin film can be compared relatively with that in the three-dimensional solid film because the q-range at SAXS and SANS measurements for each specimen was identical.

H/D segregation effects have been observed at the film surface.[22] In general, H/D segregation at the film surface is caused by annealing the film for a long time above T_g. When the two-dimensional ultrathin film was prepared by the water casting method, solvent evaporated for a few seconds at room temperature. It is, therefore, reasonable to consider that the H/D segregation in the two-dimensional ultrathin film does not occur in such a short time at room temperature below T_g. This issue is important and will be further examined.

Two times of radius of gyration, $\langle S^2\rangle^{1/2}{}_{3D}$, is regarded as the representative dimension of a polymer chain. We define a parameter D $(=t/(2\langle S^2\rangle^{1/2}{}_{3D}))$ as the ratio of the thickness, t, of the two-dimensional ultrathin film to the dimension of the polymer chain in the three-dimensional solid state. Therefore, the magnitude of D is a measure of the deformation of a polymer chain along the direction perpendicular to the film surface, when the magnitude of t becomes comparable or smaller than $2\langle S^2\rangle^{1/2}{}_{3D}$. Therefore, the magnitude of D will be used as a measure of the degree of two-dimensionality of the film. A decrease in D means that the film becomes closer to a perfect two-dimensional one in which all polymer chains lie on a plane.

Figure 1 shows the D dependence of R_S $(=\langle S^2\rangle^{1/2}{}_{2D\cdot II}/\langle S^2\rangle^{1/2}{}_{3D})$, which is defined as the ratio of the evaluated radius of gyration of a polymer chain in the two-dimensional ultrathin film to that in the three-dimensional solid film. R_S was larger than unity and increased with decreasing D, indicating that a polymer chain in the two-dimensional ultrathin film was expanded along the direction parallel to the film surface.

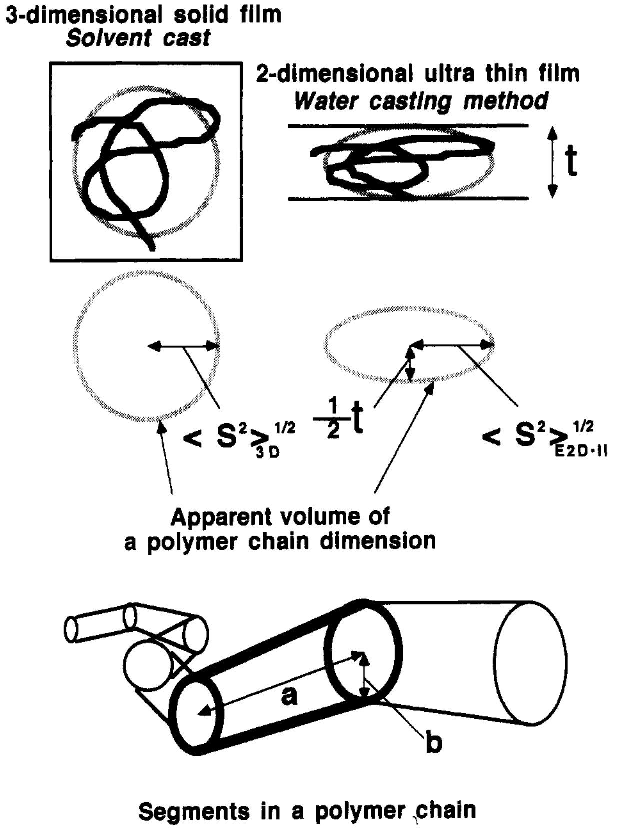

Figure 2. Schematic model of apparent volume of a polymer chain dimension and segment of a polymer chain.

In order to discuss the expansion of a polymer chain in the two-dimensional ultrathin film, let us consider the conformation of a polymer chain in an equilibrium two-dimensional solid state. The equilibrium two-dimensional state means that an individual polymer chain in it has minimum free energy. An individual polymer chain in an equilibrium three-dimensional solid state behaves as an unperturbed chain, because self-excluded volume effect is screened by the presence of monomers from different chains. As described in the Introduction, the radius of gyration of a chain along the direction parallel to the two-dimensional film surface should be equal to the radius of gyration in the three-dimensional solid state, if the polymer chain is an unperturbed Gaussian state. Here, we must consider whether a polymer chain in the equilibrium two-dimensional solid state behaves as an unperturbed chain. However, a successful theory for polymer chain conformation in a two-dimensional solid state has never been yet found. Then, we will roughly estimate the polymer chain conformation on the basis of the internal filling fraction of a polymer chain as discussed for one-dimensional system by de Gennes.[23] The internal filling fraction, Φ_{int}, of a freely jointed chain in an equilibrium state is the fraction of the volume occupied by segments from the same chain in the apparent volume of a chain dimension. Thus, the upper limit of Φ_{int} is unity.

Figure 2 shows the schematic model for the apparent volume of a chain and the segments. In order to distinguish from the evaluated radius of gyration, $\langle S^2\rangle^{1/2}{}_{2D\cdot II}$, in the two-dimensional ultrathin film prepared by the water casting method, $\langle S^2\rangle^{1/2}{}_{E2D\cdot II}$ is now defined as the radius of gyration along the direction parallel to the film surface in an equilibrium two-dimensional state. As described in the Experimental Section, the evaluated radius of gyration, $\langle S^2\rangle^{1/2}{}_{3D}$ should be equal to the radius of gyration in an equilibrium three-dimensional state. The apparent volumes of a chain in the three-dimensional and two-dimensional states were calculated representatively as the sphere with radius of $\langle S^2\rangle^{1/2}{}_{3D}$ and the ellipsoid with a semiminor axis of $(1/2)t$ and semimajor axis of $\langle S^2\rangle^{1/2}{}_{E2D\cdot II}$, respectively. Thus, Φ_{int} in the equilibrium three-dimensional solid state, $\Phi_{int(3D)}$, is expressed by eq 4

$$\Phi_{int(3D)} \cong \frac{\pi b^2 a N}{\frac{4}{3}\pi\langle S^2\rangle^{3/2}{}_{3D}} \tag{4}$$

where a and b are length and cross-sectional radius of a segment, respectively. N is the number of segments in a polymer chain. Also, Φ_{int} in an equilibrium two-dimensional solid state, $\Phi_{int(2D)}$, is expressed by eq 5

$$\Phi_{int(2D)} \cong \frac{\pi b^2 a N}{\frac{4}{3}\pi\langle S^2\rangle^{2/2}{}_{E2D\cdot II}\,{}^{1}/_{2}t} \tag{5}$$

Since $\langle S^2\rangle_{3D}$ is $({}^1/_6)Na^2$, $\Phi_{int(3D)}$ is proportional to $N^{-1/2}$. Therefore, $\Phi_{int(3D)}$ is smaller for larger values of N. If t is fairly large in comparison with 2 times $\langle S^2\rangle^{1/2}{}_{3D}$, $\langle S^2\rangle^{1/2}{}_{E2D\cdot II}$ should be equal to $\langle S^2\rangle^{1/2}{}_{3D}$.

Figure 3 shows a schematic representation of the t dependence of a polymer chain dimension and the internal filling fraction, Φ_{int}. It can be regarded that the two-dimensional and three-dimensional states correspond to the region of $t < 2\langle S^2\rangle^{1/2}{}_{3D}$ and $t > 2\langle S^2\rangle^{1/2}{}_{3D}$, respectively. Let us consider the case of decreasing t from the three-dimensional state to the two-dimensional state. In the region of $\Phi_{int(2D)} \ll 1$, it is reasonable to assume that $\langle S^2\rangle^{1/2}{}_{E2D\cdot II}$ is equal to $\langle S^2\rangle^{1/2}{}_{3D}$, because a polymer chain should still behave as an unperturbed chain. From eq 5, $\Phi_{int(2D)}$ increases with a decrease in t, because $\langle S^2\rangle^{1/2}{}_{E2D\cdot II}$ is constant in this thickness range. When the $\Phi_{int(2D)}$ approaches unity, $\langle S^2\rangle^{1/2}{}_{E2D\cdot II}$ should start to increase with decreasing t, because the number of contacts among segments in a polymer chain must strikingly increase. However, we do not know the value of $\Phi_{int(2D)}$ above which $\langle S^2\rangle^{1/2}{}_{E2D\cdot II}$ starts to increase. Here we assume that $\langle S^2\rangle^{1/2}{}_{E2D\cdot II}$ starts to increase when the $\Phi_{int(2D)}$ reaches unity. Then, we define t_c as the critical thickness in the equilibrium two-dimensional solid state for the case that $\Phi_{int(2D)}$ just reaches unity. Thus, in the case of $t > t_c$, $\langle S^2\rangle^{1/2}{}_{E2D\cdot II}$ is equal to $\langle S^2\rangle^{1/2}{}_{3D}$. In this case, eq 6 is given by eq 5

$$1 \cong \frac{\pi b^2 a N}{\frac{3}{4}\pi\langle S^2\rangle^{2/2}{}_{E2DII}\frac{1}{2}t_c} \tag{6}$$

Since $\langle S^2\rangle_{E2D\cdot II}$ is $({}^1/_6)Na^2$ in this case, eq 7 is obtained.

$$t_c \cong 16\frac{b^2}{a} \tag{7}$$

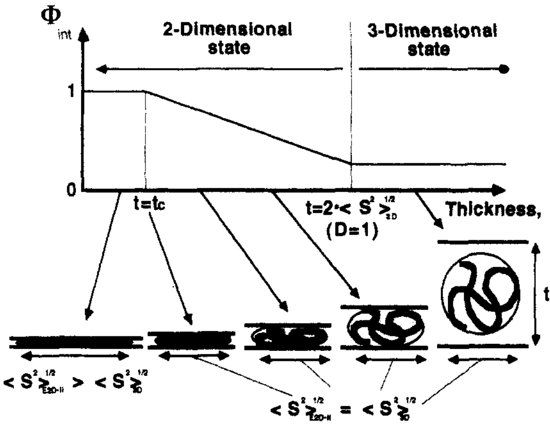

Figure 3. Thickness, t, dependence of internal filling fraction, Φ_{int} and dimension of a polymer chain along the direction parallel to the film surface.

The statistical segment length of an unperturbed PS chain was calculated to be about 2.0 nm from a characteristic ratio, $\langle S^2\rangle^{1/2}{}_{3D}/Na^2$, of 10.6.[24] The statistical segment length corresponds to the segment length, a, for a freely jointed random chain exhibiting the same statistical property as an unperturbed PS chain. Also, the cross-sectional radius of a segment, b, is calculated to be about 0.46 nm from the molecular weight of a segment. The magnitude of t_c for the two-dimensional ultrathin film of PS is estimated to be about 1.7 nm, by substitution of the values of a and b to eq 7. Therefore, in the case of the equilibrium two-dimensional solid state, the estimated limiting thickness above which the radius of gyration of a PS chain along the direction parallel to the film surface could be equal to that of an unperturbed chain is 1.7 nm. Of course, we should regard the value of 1.7 nm as a rough approximated value, because Φ_{int} was defined as the mean volume fraction of a chain in the apparent volume of itself without considering the density fluctuation of segments due to correlation among segments in a chain. And also, as mentioned before, $\langle S^2\rangle^{1/2}{}_{E2D\cdot II}$ should start to increase with decreasing t, before the $\Phi_{int(2D)}$ reaches unity. Here, we consider that the estimated value of t_c is close to the real value of limiting thickness above which the radius of gyration of a PS chain along the direction parallel to the film surface is equal to that of an unperturbed chain. The accurate value of t_c should be estimated by another approach, for example, Monte Carlo simulation. As shown in Table I, $\langle S^2\rangle^{1/2}{}_{2D\cdot II}$ was larger than $\langle S^2\rangle^{1/2}{}_{3D}$, though the film thickness was much larger than t_c of about 1.7 nm. Therefore, it can be reasonably concluded that the two-dimensional ultrathin film prepared by water casting method is in an unequilibrium state. The unequilibrium aggregation state should be formed during the film formation process, that is, entangled polymer chains may be expanded by spreading of the solution on the water surface and then frozen in the glassy state with an expanded conformation owing to the rapid dissipation of solvent into the air and/or water phase. Therefore, R_S $(=\langle S^2\rangle_{2D\cdot II}{}^{1/2}/\langle S^2\rangle_{3D}{}^{1/2})$ may be used to measure the degree of unequilibrium state of the film. As shown in Figure 1 and Table I, the D dependence of R_S seems to be consistent with respect to the magnitudes of both M_w of PS and the thickness of films, indicating that the degree of unequilibrium state of the film strongly depends on D.

Figure 4 shows the D dependence of R_v which is the ratio of the apparent volume of a PS chain in the two-dimensional ultrathin film to that in the three-dimensional solid film. The apparent volumes of a PS chain in the two-dimensional ultrathin film, V_{2D}, and that in the three-dimensional solid film, V_{3D}, were calculated by the eqs 8 and 9, respectively.

$$V_{2D} = \frac{4}{3}\pi\langle S^2\rangle^{2/2}{}_{2D\cdot II}\frac{1}{2}t \tag{8}$$

$$V_{3D} = \frac{4}{3}\pi\langle S^2\rangle^{3/2}{}_{3D} \tag{9}$$

As shown in Figure 4, R_v $(=V_{2D}/V_{3D})$ decreased with D, especially when D is less than unity. Since the apparent volume of a PS chain corresponds to the volume occupied not only by a noticed chain but also by the surrounding

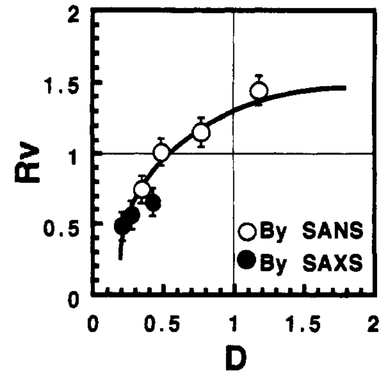

Figure 4. Relation between R_V and D. R_V is the ratio of apparent volume of a chain in two-dimensional ultrathin film to that in three-dimensional solid film.

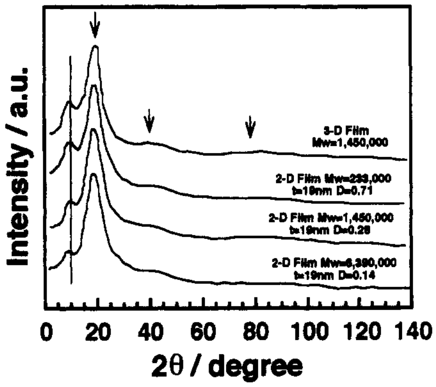

Figure 5. Wide angle X-ray scattering intensity profiles, $I_{ex}(2\theta)$, of two-dimensional ultrathin film and three-dimensional solid film.

chains, a decrease of the apparent volume should result in a decrease of the degree of interpenetration and the entanglement among polymer chains. As a result, a polymer chain in the two-dimensional ultrathin film becomes more isolated with decreasing D. It should be noticed that the number of entanglements in the two-dimensional ultrathin film should have important effects on the mechanical properties such as modulus, creep behavior, stress relaxation phenomena, etc.

Molecular Packing in Two-Dimensional Ultrathin Film. The corrected wide angle X-ray scattering intensity profiles, $I_{ex}(2\theta)$s, of the two-dimensional ultrathin film measured by the symmetrical-transmission and symmetrical-reflection technique were completely comparable. Therefore, it is reasonable to conclude that the short range correlations of atoms along parallel and perpendicular directions of the film surface are identical.

Figure 5 shows $I_{ex}(2\theta)$ values, measured by the symmetrical transmission technique, for the two-dimensional ultrathin film and the three-dimensional solid film. Since $I_{ex}(2\theta)$ values of the three-dimensional solid films with M_w of 233 000, 1 450 000, and 6 390 000 were identical, only $I_{ex}(2\theta)$ of the three-dimensional solid film with M_w of 1 450 000 was shown as an example. In this three-dimensional solid film of PS, characteristically broadened amorphous halos were observed at 2θ of about 10°, 20°, 40°, and 80°. These halos have been assigned as follows.[25,26] The halo at 10° is the so-called "prepeak", which may be related to the existence of the main chain. However, the origin of the halo at 10° is not well understood. The halo at 20° corresponds to the contribution of the distance between intermolecular methylene–methylene, methylene–phenyl, and phenyl–phenyl groups. The halo at 40° is due to the intermolecular contribution and second neighbor C–C–C bond. The halo at 80° corresponds to the first neighbor C–C bond as a main contribution and the second neighbor C–C bond as a subsidiary contribution. In this case of the two-dimensional ultrathin film, the WAXS intensity of the halo at 10° was weaker than that of the three-dimensional solid film. This indicates that the aggregation structure of the two-dimensional ultrathin film is different from that of the three-dimensional solid film.

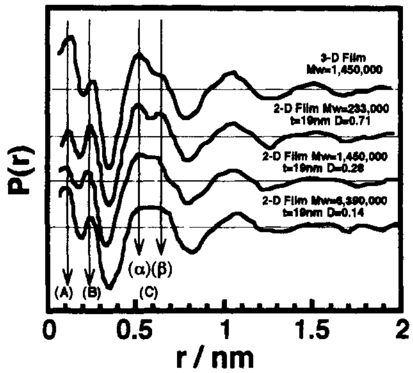

Figure 6. RDF, $P(r)$, of two-dimensional ultrathin film and three-dimensional solid film.

Figure 6 shows RDF, $P(r)$ values for the two-dimensional ultrathin film and the three-dimensional solid film. $P(r)$ values were calculated on the basis of wide angle X-ray scattering profiles shown in Figure 5. The characteristic peaks were observed at about 0.15, 0.25, and 0.50–0.65 nm, being marked by A, B, and C, respectively. The A, B, and C peaks correspond to the distance of the nearest neighbor C–C bond, the second neighbor C–C bond, and intermolecular packing in an amorphous state, respectively. The intermolecular packing in the polymer amorphous state should correspond to the monomer–monomer packing between chains and in a chain. The q range of WAXS measurements in this study was not so wide. The termination effect mainly causes the error at small r–range. For evaluating $P(r)$, the error became larger in smaller than the 0.2-nm range. However, the error from the termination effect almost disappeared in the more than 0.2-nm range, because peak B at 0.25 nm corresponding to second neighbor C–C–C bonds was equivalent in any sample. Therefore, it can be considered that peak (C) was accurate enough for relative comparison between the two-dimensional ultrathin film and the three-dimensional solid film. The shape of peak C corresponding to the intermolecular distance in the three-dimensional solid film looks like a triangle inclining toward the short distance side, which is similar to the case for PS bulk.[27,28] It is considered that peak C consists of two peaks α and β which correspond to distances of about 0.5 and 0.65 nm, respectively. Peaks α and β might correspond to intermolecular distance in tight packing and relatively loose packing states, respectively. As shown in Figure 6, the intensity of the α peak became weaker and that of the β peak became relatively stronger with a decrease of D in the case of the two-dimensional ultrathin film. This result also indicates that the average intermolecular packing in the two-dimensional ultrathin film was looser than that in the three-dimensional solid film. The loose packing of polymer chains in the two-dimensional ultrathin film may arise from the unequilibrium formation process of the film as discussed in the previous section. That is, since the rapid dissipation of solvent does not allow sufficient time for polymer chains to obtain a stably-relaxed conformation during the water casting process, the intermolecular packing in the two-dimensional ultrathin film remains loose compared to that in the three-dimensional solid state.

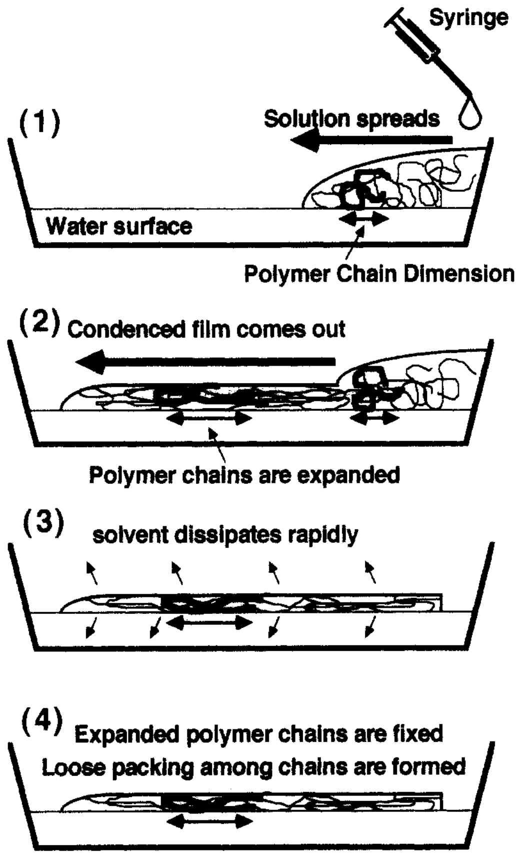

Figure 7. Schematic representation for the formation mechanism of two-dimensional ultrathin film by the water casting method.

The entanglement among polymer chains is an important factor in the formation process of the two-dimensional ultrathin film by the water casting method, as reported previously.[11] Also, the expanded polymer chains in the two-dimensional ultrathin film are fixed by rapid dissipation of solvent. Figure 7 shows a schematic representation of the formation process of the two-dimensional ultrathin film by the water casting method. Film formation consists of the following: (1) solution spread with initial dissipation of solvent; (2) condensed solution film was formed with the expansion of polymer chains; (3) solvent rapidly dissipated owing to the thin state of the system; (4) dried film formed with fixation of expanded polymer chains and a slight relaxation in packing of polymer chains.

This unequilibrium formation of two-dimensional ultrathin film provides remarkable characteristic aggregation structure such as the expanded and loosely packed chains, especially in the case of a small value of D. Therefore, the chain conformation in the two-dimensional ultrathin film is unstable owing to the small conformational entropy, so that the conformation has a tendency to change into that of the three-dimensional unperturbed chain. How to freeze stably the conformation of polymer chains in the two-dimensional ultrathin film remains an unsolved problem, although it is an important one. This problem is currently being examined to apply the two-dimensional ultrathin film as engineering devices.

Conclusion

A PS chain in the two-dimensional ultrathin film, prepared by the water casting method, was expanded along the direction parallel to the film surface. The degree of entanglement among polymer chains in the two-dimensional ultrathin film was less than that in the three-dimensional bulk polymer. The molecular packing in the two-dimensional ultrathin film was looser than that in the three-dimensional solid film. This characteristic aggregation structure in the two-dimensional ultrathin film was strongly related to the unequilibrium formation process due to rapid dissipation of solvent.

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(29) Certain commercial equipment, instruments, or materials are identified in this paper in order to adequately specify the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.