BUTTERWORTH
HEINEMANN

Polymer Vol. 36 No. 3, pp. 549–557, 1995

0032-3861/95/$10.00+0.00

Non-equilibrium characteristics of a two-dimensional ultrathin film prepared by the water casting method

Kenshiro Shuto, Yushi Oishi* and Tisato Kajiyama†
Department of Chemical Science and Technology, Faculty of Engineering, Kyushu University, 6-10-1 Hakozaki, Higashi-ku, Fukuoka 812, Japan
(Received 23 March 1994; revised 24 May 1994)

A two-dimensional ultrathin film was defined as being a film thinner than the dimension of an unperturbed Gaussian chain in the three-dimensional state. The segment density of an unperturbed chain in equilibrium in the two-dimensional solid state was investigated using a Monte-Carlo simulation. When the film thickness exceeds 30% of twice the radius of gyration of a three-dimensional unperturbed chain, the segment density is not particularly high in comparison with the three-dimensional state. This means that a polymer chain will behave as a two-dimensional unperturbed chain in the equilibrium state of a two-dimensional ultrathin film, as in a three-dimensional solid state. Therefore, the excess expansion of a polymer chain in a two-dimensional ultrathin polystyrene film with a thickness comparable to twice the radius of gyration of a three-dimensional unperturbed chain might arise from non-equilibrium characteristics. In addition, the relaxation behaviour of a two-dimensional ultrathin film of a styrene–butadiene–styrene (SBS) triblock copolymer was investigated by transmission electron microscopy. The two-dimensional ultrathin SBS film contracted and decomposed into two phases (polystyrene and polybutadiene) from the one phase right after the film preparation. This indicates that the two-dimensional ultrathin film was in a distinct non-equilibrium state right after spreading a solution on the water surface.

(Keywords: ultrathin polymeric film; Monte-Carlo simulation; SBS triblock copolymer)

INTRODUCTION

A flexible polymer chain in the three-dimensional amorphous bulk state behaves as an unperturbed ideal Gaussian chain[1–3]. Thus, it is very important and interesting to study the case in which the film thickness is smaller than the dimension of an unperturbed chain. This is because a polymer chain in such a case is restricted to a small spatial dimension perpendicular to the film surface and, therefore, the conformational entropy of an individual chain is smaller than that in the three-dimensional solid state[4,5]. Therefore, it is expected that the aggregation structure and mechanical properties of such an ultrathin film will be quite different from those of the three-dimensional amorphous, solid, thick film. In order to distinguish a film thinner than the dimension of an unperturbed chain from that of a three-dimensional solid film, we have defined the former as a two-dimensional ultrathin film.

The conformation of an isolated polymer chain in the two-dimensional state has been investigated theoretically and numerically for the case in which a polymer chain was confined between two plates[5–9]. In the case of an unperturbed Gaussian chain which has no excluded volume, the segment density distribution in one direction (e.g. parallel to the plate) is independent of that in the other direction (e.g. perpendicular to the plate). This means that the segment density distribution in the direction parallel to the plate does not change, even if the polymer chain is restricted to a small spatial dimension perpendicular to the plate. Thus, the radius of gyration of an unperturbed chain in the direction parallel to the plate should be equal to that of an unperturbed chain in the three-dimensional state. On the contrary, when a perturbed chain with an excluded volume exists in the two-dimensional state, the perturbed chain dimension in the direction parallel to the plate becomes larger than the perturbed chain dimension in the three-dimensional state, due to the difference between the excluded volume effects in the direction perpendicular to the plate to that in the direction parallel to the plate, because of the restriction of the excluded volume effect to the region perpendicular to the plate.

In contrast to these isolated polymer chain systems, the conformation of a polymer chain in a two-dimensional ultrathin film, in which the polymer chains are aggregated in an entangled fashion, has not been investigated. The present authors have previously reported the aggregation structure of a two-dimensional ultrathin polystyrene (PS) film prepared by a water casting method[10,11]. Neutron and small-angle X-ray scattering analyses revealed that the radius of gyration in the direction parallel to the film surface was larger than the radius of gyration of the three-dimensional unperturbed chain. It was inferred from this that the excess expansion of a PS chain in the two-dimensional

---

* Present address: Department of Applied Chemistry, Saga University, 1 Honjo-machi, Saga 840, Japan

† To whom correspondence should be addressed

ultrathin film mainly originated from the following two causes. First, the excluded volume effect is greater in the two-dimensional than in the three-dimensional state because of the higher segment density of the chains in the former. The high segment density is due to the restricted dimension of the polymer chains which causes a decrease in the apparent volume of the chain and an increase in the number of contact segments in the chain. The second reason is the freezing of the expanded chains during film formation, resulting from both the expansion of the solution and the rapid dissipation of the solvent from the thin film surface. This means that the two-dimensional ultrathin film is in a non-equilibrium state. The details of these speculations will be explained below.

The purpose of this paper is (1) the numerical estimation of the segment density in an unperturbed Gaussian chain in the two-dimensional solid state, which is strongly related to the excluded volume effect, and (2) the demonstration of the non-equilibrium characteristics of a two-dimensional ultrathin film composed of a polymer chain which can relax into the equilibrium state, even if the two-dimensional ultrathin film is in a non-equilibrium state. The number of contacts between two segments in a chain (corresponding to the segment density) was estimated by a Monte-Carlo simulation. The relaxation behaviour of a two-dimensional ultrathin film of a styrene–butadiene–styrene (SBS) triblock copolymer was also investigated by transmission electron microscopy in order to confirm the non-equilibrium characteristics of a two-dimensional ultrathin film prepared by a water casting method.

EXPERIMENTAL

Estimation of the number of contacts between two segments in an unperturbed chain based on a Monte-Carlo simulation

An unperturbed freely jointed chain, which had the same statistical characteristics as an unperturbed polystyrene chain, was used as the model for a polymer chain. The statistical segment length of an unperturbed PS chain was calculated to be ~ 2.0 nm from the characteristic ratio ($\langle R^2\rangle^{0.5}$: nb^2, where $\langle R^2\rangle^{0.5}$, n and b are the root mean square of the end-to-end distance of the unperturbed chain, the number of C–C bonds in the main chain and the length of the C–C bond, respectively), is equal to 10.6 for a PS chain[12]. The number of segments in the model chains were 50, 100, 500, and 2000, which corresponded to PS chains with weight-average molecular weights of $\sim$40 000, 80 000, 400 000 and 1 600 000, respectively. *Figure 1* shows the model chain for the Monte-Carlo simulation and the binary cluster integral, β, corresponding to the effective excluded volume of a segment. The binary cluster integral should be equal to eight times the effective volume of a segment. The volume of a segment can be calculated from the binary cluster integral in an athermal solvent. On the basis of perturbation theory, the value of the binary cluster integral of PS was estimated to be ~ 0.3 nm for each monomer[13]; the radius of the sphere corresponding to the volume of a statistical segment was estimated to be ~ 0.4 nm by using this value for the binary cluster integral. However, a more accurate value of the binary cluster integral cannot be evaluated from perturbation theory. Thus, in order to investigate the effect of the size of the segment on the segment density, values of 0.2, 0.4, 0.6 and 0.8 nm were used for the radius of a segment volume for the model chains used in this study (as described above).

Figure 2 shows a schematic representation of the Monte-Carlo simulation process. The process is as follows:

(1) An unperturbed Gaussian model chain was generated in two-dimensional free space, confined within two plates separated by a distance, t (referred to as the 'thickness of the two-dimensional state' in this paper). First, one of the ends of the chain was determined at a random position along the direction perpendicular to the plate. The chain was then grown step-by-step along a random direction in the allowed two-dimensional space.

(2) The number of contacts between two segments of the model chain (N) was counted. In this case, it was taken that the segment of the model chain had a volume corresponding to the volume of a segment in a real polymer chain. The end-to-end distance, and the projected length of the end-to-end distance onto the xy plane (the film surface), R_p, of the model chain were also estimated.

In this calculation 10 000 chains were generated for each condition of N and t, and then the average number of contacts between two segments of the model chain was estimated as a function of t. A large number of

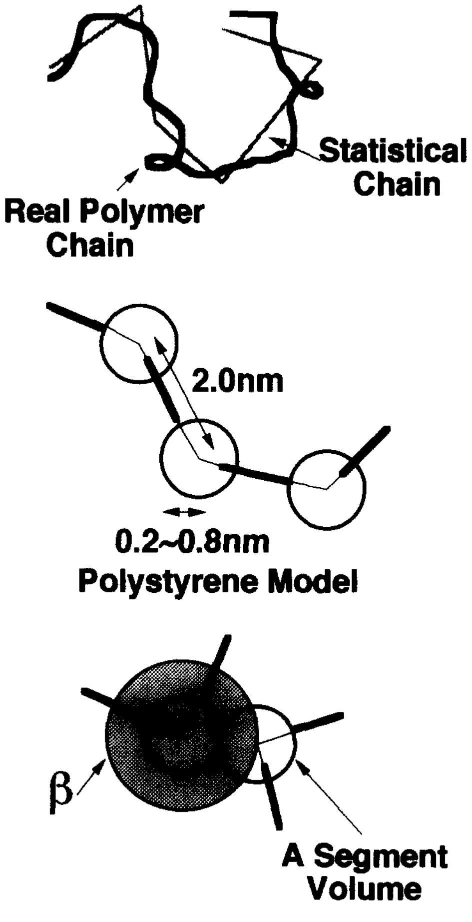

Figure 1 A model chain having the same statistical characteristics as an unperturbed polystyrene chain, used for the Monte-Carlo simulation (top and middle), and the binary cluster integral, β, (bottom) with the latter corresponding to the effective excluded volume

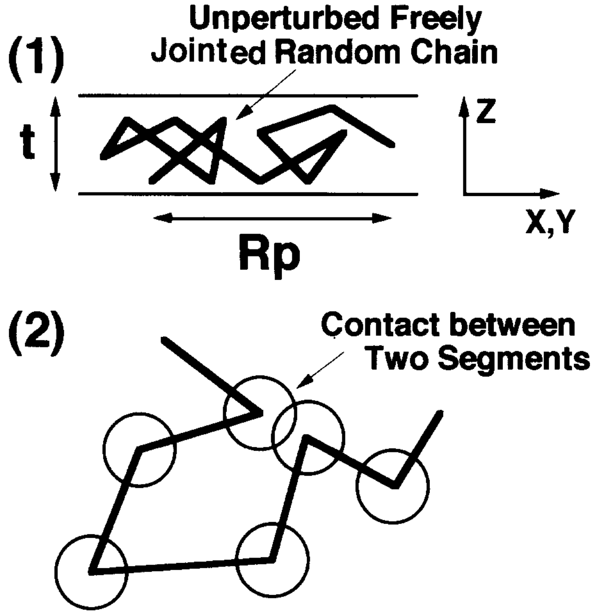

Figure 2 Schematic representation of the Monte-Carlo simulation: (1) generation of an unperturbed chain; (2) counting of the number of contacts between two segments

contacts between two segments of the model chain would indicate that real polymer chains do not behave as an unperturbed Gaussian chain.

Estimation of the relaxation behaviour of a two-dimensional ultrathin SBS film prepared by a water casting method

Micro-Brownian motion does not occur in the PS solid state at room temperature because the glass transition temperature, T_g, of PS is ~380 K. On the contrary, micro-Brownian motion occurs in the polybutadiene (PB) solid state at room temperature, because the T_g of PB is ~180 K. The polymer chains in a film prepared from styrene–butadiene–styrene triblock copolymer (SBS) will be able to relax to the equilibrium state owing to the micro-Brownian motion of the PB chain if the film is in the non-equilibrium state immediately after preparation.

The samples in this study were prepared using commercially available SBS with a number-average molecular weight, M_n, of 91 000 and a styrene/butadiene weight ratio of 1.5 (Japan Synthesis Rubber Co.). The two-dimensional ultrathin film was prepared by a water casting method, i.e. by carefully spreading a single droplet of polymer solution onto a water surface[10]. The polymer solution spreads spontaneously. The solvent evaporated and the remainder of the polymer then dissolved in the water for a few seconds. A dried thin film was then formed on the water surface. Cyclohexanone solutions of 1.0 and 2.0 wt% were spread onto the surface at 293 K.

In order to estimate the relaxation behaviour of a two-dimensional ultrathin film, the holding-time dependence of the film dimension was estimated. *Figure 3* shows the estimation method used to determine the film dimension ratio, $L(TH)/L(0)$, of the two-dimensional ultrathin SBS film induced by the relaxation of SBS chains on the water surface, where $L(TH)$ is the film dimension at the holding time of TH. Small metal pieces were put on the film surface as markers immediately after the formation of the two-dimensional ultrathin SBS film on the water surface. In order to estimate the $L(TH)/L(0)$ ratio of the two-dimensional ultrathin SBS film, the marker positions were measured using a cassette meter. After holding the thin film on the water surface for periods of 0, 1, 3 and 48 h at 293 K, the two-dimensional ultrathin film was transferred onto an electron microscope grid. *Figure 4* shows a schematic representation of the dyeing apparatus that was used. In order to hold the aggregation structure without relaxation, the samples were maintained in a sample holder cooled by liquid nitrogen. Osmic acid vapour was then introduced into the sample

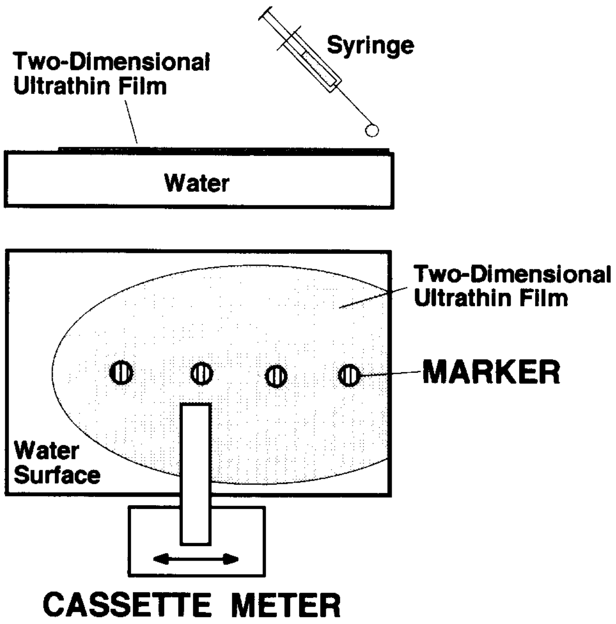

Figure 3 Schematic representation of the estimation method used to determine the film dimension ratio, $L(TH)/L(0)$ of the two-dimensional ultrathin SBS film held on the water surface

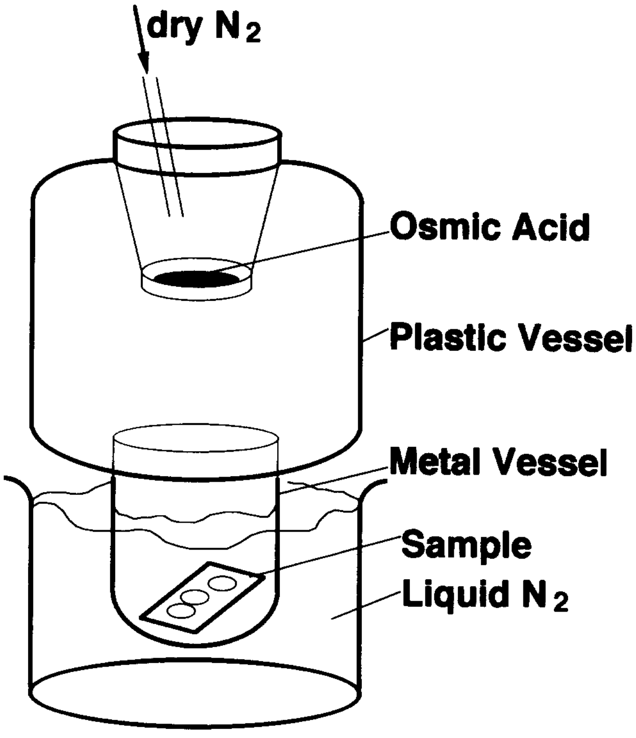

Figure 4 Schematic representation of the technique used for dyeing with osmic acid; the sample was cooled by liquid nitrogen in order to freeze the aggregation structure of the film

holder for 4 h in order to stain the butadiene segment positively. Bright field images were taken with a transmission electron microscope (Hitachi, H-7000) in order to analyse the microphase separated structure. Fourier transform patterns of the bright field images were also obtained using an imaging analyser.

RESULTS AND DISCUSSION

Possible origins of the polymer chain expansion in two-dimensional ultrathin films

In the two-dimensional ultrathin films prepared by the water casting method, the radius of gyration of the PS chain in the direction parallel to the film surface was larger than the radius of gyration of a three-dimensional unperturbed chain[10,11]. When the polymer chain is in the unperturbed state, the polymer chain dimension parallel to the film surface in two-dimensional space is equal to that in the three-dimensional state. Thus, we concluded that the PS chain in the two-dimensional ultrathin film was not in an unperturbed state. Why would the polymer chain behave as a non-ideal chain in the two-dimensional ultrathin film? Our aim in this paper is to consider the origin of the excess expansion of the PS chain in a two-dimensional ultrathin film.

The real situation concerning the aggregation structure is very complex, since many non-ideal chains are interacting with each other in two-dimensional space. Thus, it is not possible to completely discuss the two-dimensional aggregation state of a polymer chain with all its interacting factors with other polymer chains. Therefore, we concentrated on the main factors concerning the excess expansion of polymer chains in a two-dimensional aggregation state. Before we discuss these, it will be useful to draw a distinction between two antagonistic situations, namely the equilibrium and non-equilibrium states of the two-dimensional solid state. The equilibrium two-dimensional state denotes the state in which an individual polymer chain has the minimum free energy as a two-dimensional polymer chain. If a two-dimensional ultrathin film is in the equilibrium state, we should consider the origin of the excess expansion of a polymer chain in the two-dimensional aggregated polymer system to be unrelated to the film formation method used. If a two-dimensional ultrathin film is in a non-equilibrium state we may consider the reason for the non-equilibrium aggregation structure, with an excess expansion of the chain, to be due to the film formation method that is employed.

When a two-dimensional ultrathin film is in the equilibrium state, the origins of the excess expansion of the polymer chain were thought to be the following. The first is the excluded volume effect caused by the high segment density of a polymer chain. An individual polymer chain in the three-dimensional amorphous solid state behaves as an unperturbed Gaussian chain because the excluded volume is screened by the surrounding segments of the other chains. This concept is supported by the fact that the segment density of an unperturbed Gaussian chain in a three-dimensional state is very low[14]. However, in the two-dimensional state, the segment density of an unperturbed chain is high because the chain is restricted to a small spatial dimension which causes a decrease in the apparent volume of the chain and an increase in the number of contacts amongst segments in the chain. The high segment density of a two-dimensional unperturbed chain may not cause a real polymer chain to behave as an unperturbed chain, but will make a real polymer chain expand in the direction parallel to the film surface, even in the aggregated solid state. The second explanation is the interaction between the polymer chain and the water surface. When an isolated polymer chain is attracted to the water surface (e.g. a polymer with hydrophilic group), the individual polymer chain has a tendency to lie on the water surface and expand[15]. However, in the case of a PS chain which has no interaction with the water surface, the individual PS chain collapses to monomolecular particles and its lateral size becomes smaller than the unperturbed chain dimension[16]. Thus, it is considered that the PS chains will shrink rather than expand through an interaction with the water surface, even if the polymer chains aggregate in the two-dimensional state.

Therefore, if the two-dimensional ultrathin film is in the equilibrium state, we believe that the origin of the excess expansion of the polymer chain is mainly due to the excluded volume effect, resulting from the high density of the segment. This problem is too complex to be discussed here completely. As a first step for the investigation of the excluded volume effect in the two-dimensional aggregation state, the number of contacts between two segments of corresponding segment density was estimated on the basis of a Monte-Carlo simulation. A large number of contacts between two segments in the chain means that the allowed conformation of the polymer chain is too small to behave as an unperturbed Gaussian chain.

If the two-dimensional ultrathin film is in a non-equilibrium, two-dimensional solid state form, the origin of the excess expansion of the polymer chain lies in the preparation process of the non-equilibrium aggregation structure of the polymer chains. A non-equilibrium aggregation structure may be formed by the rapid dissipation of the solvent during the water casting process and the freezing of the expanded chains. In this case, it is important to clarify that the two-dimensional ultrathin film is in a non-equilibrium state. In order to demonstrate the non-equilibrium characteristics of the two-dimensional ultrathin film, the relaxation behaviour of a two-dimensional ultrathin film of styrene–butadiene–styrene (SBS) triblock copolymer was investigated on the basis of results obtained by using transmission electron microscopy.

Number of contacts between two segments of an unperturbed Gaussian chain in the two-dimensional state

We investigate the segment density of an unperturbed Gaussian chain in the two-dimensional state by the estimation of the number of contacts between two segments on the basis of a Monte-Carlo simulation. The high segment density of a two-dimensional unperturbed Gaussian chain may not cause a real polymer chain to behave as an unperturbed chain, but will make a real polymer chain expand in the direction parallel to the film surface, even in the aggregated solid state.

The parameter representing the two-dimensionality of the system will be considered below. In the three-dimensional state, the representative dimension of a

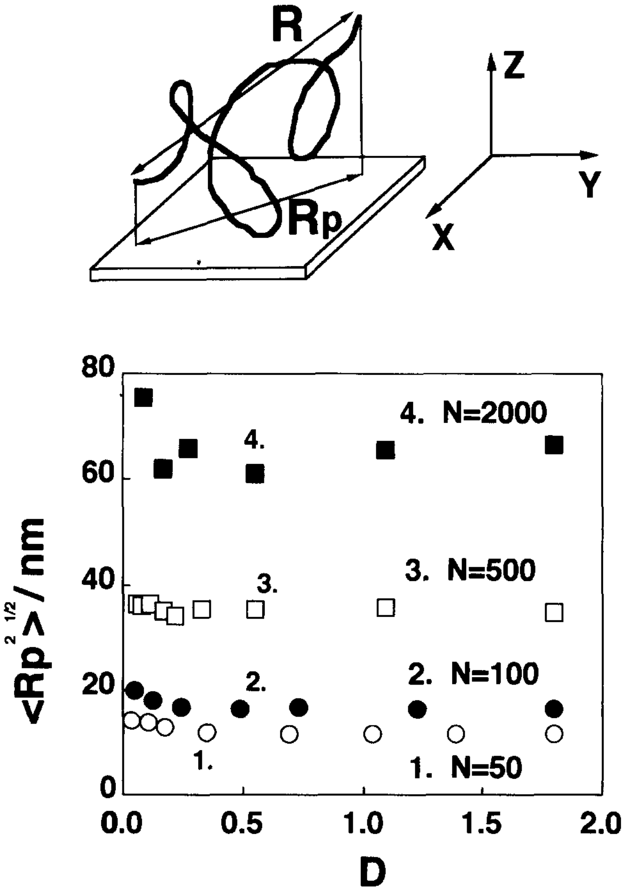

Figure 5 Schematic model of R_p, being the component length of the end-to-end distance in the xy plane (top), and the two-dimensional parameter, D, dependence of R_p shown for different values of the segment number, N (bottom)

polymer chain is regarded to be twice the radius of gyration. Therefore, a parameter D $(=t/(2\langle S^2\rangle_{3D}^{0.5}))$ was defined as being the ratio of the thickness, t, of the two-dimensional state to twice the radius of gyration, $\langle S^2\rangle^{0.5}$, of an unperturbed Gaussian chain in the three-dimensional solid state. The magnitude of D corresponds to the degree of deformation of the polymer chain in the direction perpendicular to the film surface if the magnitude of t is comparable to, or smaller than twice the radius of gyration. The magnitude of D can therefore be used as an indicator of the degree of two-dimensionality of the film. A decrease in D corresponds to an increase in two-dimensionality, with the perfect case being one in which all polymer chains prefer to be lying in a plane.

Figure 5 shows a schematic model of the projected length of the end-to-end distance onto the xy plane (the film surface), R_p, and a plot of the root mean square of R_p vs. D for different values of N. The value of R_p for an unperturbed Gaussian chain in the two-dimensional state should be equal to that in the three-dimensional state, because the segment density distribution parallel to the xy plane is independent of the z-direction, as mentioned above. In all cases of N, the magnitudes of R_p in the region where $D<1$ agree well with those of R_p in the three-dimensional state of $(D\gg 1)$. However, the magnitude of R_p for the case where $D\sim 0$ is slightly larger than that of the three-dimensional unperturbed chain. This indicates that the fraction of segments lying along the xy plane increases slightly because the thickness, t, of the film is smaller than the segment length ($a=2.0$ nm). However, this influence of the segment vector is not that remarkable. Therefore, it is reasonable to conclude that the unperturbed Gaussian chain was also generated in the two-dimensional state, since the magnitude of R_p was independent of the thickness of the system.

Figure 6 shows the D dependency of the ratio of the number of contacts between two segments of a model chain in a two-dimensional state to that in a three-dimensional one, as a function of the radius of the segment. In all cases of both N and the radius of the segment, the number of contacts between two segments remains almost constant in the region where $D>0.3$. On the other hand, the number of contacts between two segments increased drastically with a decrease in D in the region where $D<0.3$. *Figure 6*, therefore, indicates that the segment density of an unperturbed Gaussian chain in the two-dimensional state for $D>0.3$ is comparable with that in the three-dimensional state. Thus, the degree of the excluded volume effect in the two-dimensional state for $D>0.3$ should be equivalent to that in the three-dimensional state. Therefore, the excluded volume effect caused by the restricting condition of a narrow layer space may not be so remarkable in the region where $D>0.3$. This indicates that the excluded volume effect of a PS chain in the region where $D>0.3$ may be screened by the monomers of surrounding chains which exist in a similar fashion to that in the three-dimensional solid state, as mentioned in a previous section. Since $D=0.3$ is a rough critical value which indicates whether a polymer chain behaves as an unperturbed chain in the two-dimensional solid state or not, it cannot be directly considered that the polymer chains will expand in the direction parallel to the film surface in the region where $D<0.3$.

As reported previously[10,11], the PS chain in the two-dimensional ultrathin film was expanded in the direction parallel to the film surface, even in the case where the film thickness was twice the radius of gyration ($D=1$). Comparing the experimental results with the simulated results shown in *Figure 6*, the excess expansion of the PS chain in the two-dimensional ultrathin film prepared by the water casting method should not be due to the high segment density of the chains. As mentioned above, it was speculated that the origin of the excess expansion of the polymer chain in the two-dimensional ultrathin film was mainly the excluded volume effect when it was in the equilibrium state. Thus, it was inferred that the two-dimensional ultrathin film prepared by the water casting method was not in the equilibrium state. What can be said is that the possibility of the excess expansion of the polymer chain dimension being caused by the high segment density of the chains is almost negligible. In the next section, the non-equilibrium characteristics of the two-dimensional ultrathin film will be discussed on the basis of the relaxation phenomena of the two-dimensional ultrathin SBS film.

Relaxation behaviour of the two-dimensional ultrathin SBS film prepared by the water casting method

The thickness of the two-dimensional ultrathin SBS film could not be evaluated because the thickness changed

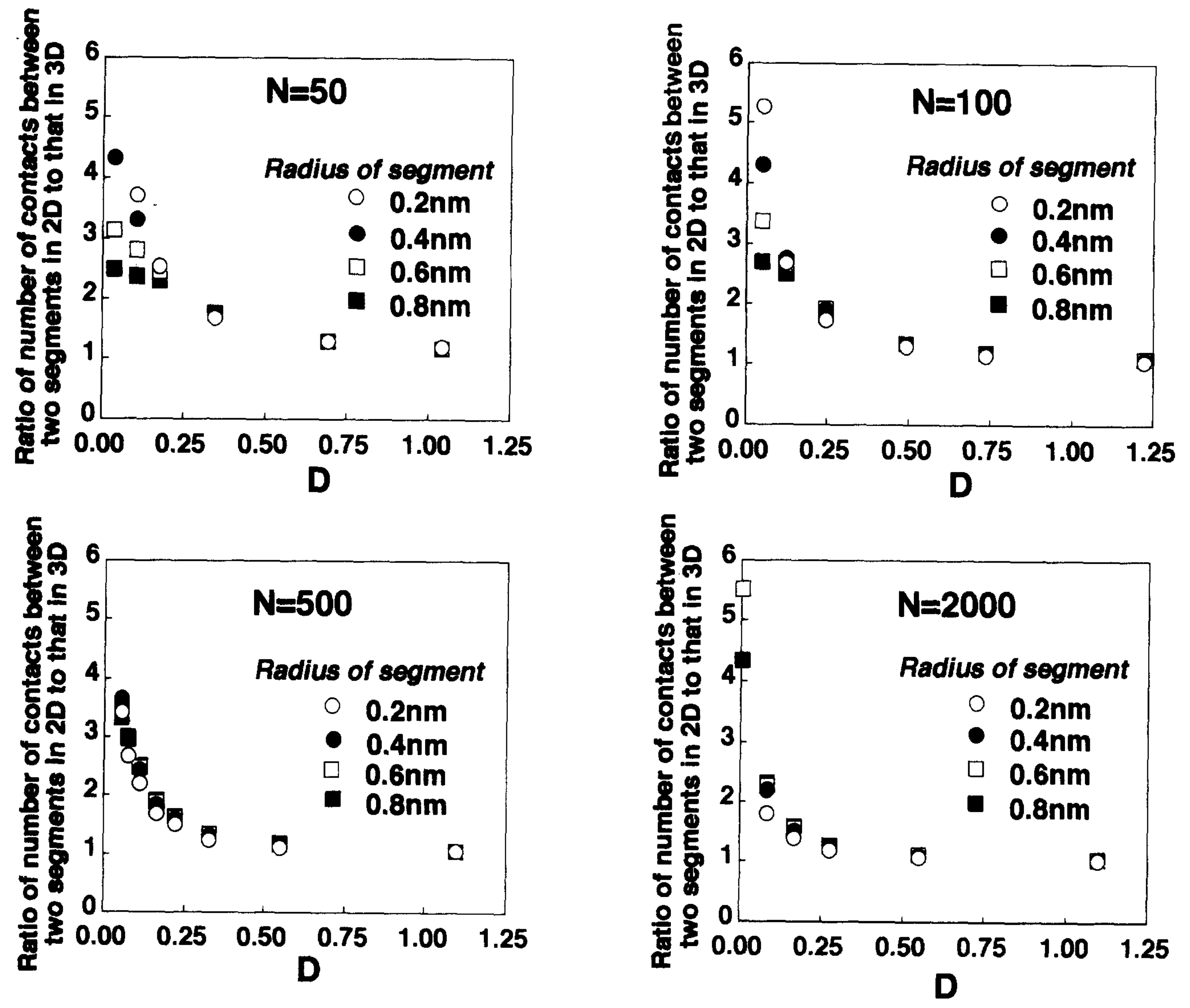

Figure 6 The two-dimensional parameter, D, dependence of the ratio of the number of contacts between two segments in a model chain in two dimensions to that in three dimensions, shown for different values of N and the segment radius

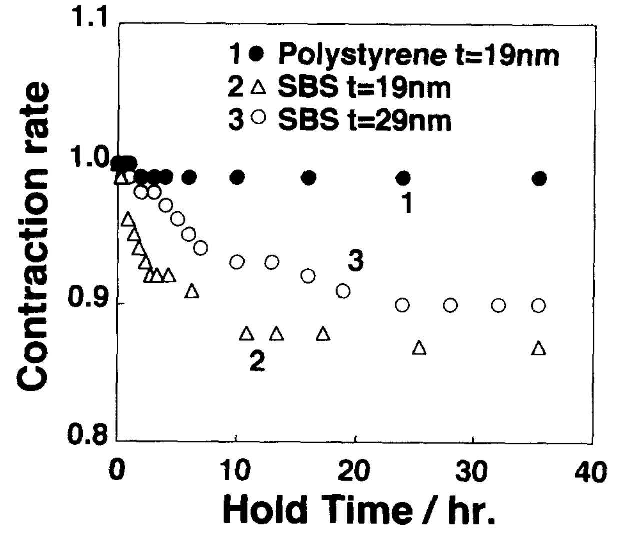

Figure 7 The holding-time dependence of the film dimension ratio, $L(TH)/L(0)$, of the two-dimensional ultrathin SBS and PS films on the water surface

with the holding time of the film on the water surface. On the basis of an X-ray interference method, the thicknesses of the two-dimensional ultrathin PS films prepared from 1.0 and 2.0 wt% solutions were estimated to be 19 and 29 nm, respectively[10]. Since the spread area of a SBS solution on the water surface was equal to that of a PS solution, it can be assumed that the thickness of the two-dimensional ultrathin SBS film was comparable to that of the corresponding PS film prepared from a spreading solution of the same concentration. Therefore, the thickness of the SBS films immediately after preparation from spreading solutions of 1.0 and 2.0 wt% were assumed to be 19 and 29 nm, respectively. Since the radius of gyration of an unperturbed SBS chain with a molecular weight of 91 000 was calculated to be ~10.2 nm from the characteristic ratio of the PS[12] and PB[17] chains, the two-dimensional parameter, D, of the films with thicknesses of 19 and 29 nm were ~0.9 and 1.4, respectively.

Figure 7 shows the film dimension ratio, $L(TH)/L(0)$, for the two-dimensional ultrathin SBS films and PS film

Figure 8 Electron microscope bright field images of the two-dimensional ultrathin SBS films after dyeing with osmic acid; black portions correspond to the polybutadiene phase

on the water surface as a function of the holding time. The size of the two-dimensional ultrathin PS film did not change with holding for a period of 40 h. On the other hand, the sizes of both of the two-dimensional ultrathin SBS films decreased after film formation and reached an equilibrium size after a holding time of 30 h at 293 K. This may indicate that the expanded polymer chains of the SBS thin film shrink immediately after film formation owing to a conformational relaxation of the chains because the subphase (water) temperature is much higher than the T_g of the butadiene segments of the SBS chain. The contraction ratios, $(L(0)/L(\infty)-1) \times 100$, compared with the equilibrium states for the two-dimensional ultrathin SBS films with thicknesses of 19 and 29 nm, were 15 and 11%, respectively. These values of the contraction ratio were comparable to the degrees of expansion of the PS chains in a two-dimensional ultrathin film in the direction parallel to the film surface[10]. The fact that larger contractions were observed for thinner films supports the idea that a decrease in the film dimension is mainly caused by the relaxation of individual chain conformations.

Figure 8 shows electron microscope bright field images of the two-dimensional ultrathin SBS films at holding times, *TH*, of 0, 1, 3 and 48 h on the water surface. The SBS thin films were cooled in liquid nitrogen in order to prevent further relaxation. The black portions in the bright field images represent the PB phase, since the double-bond groups of the PB chains are selectively stained positive by the osmic acid[18]. In the bright field image of the film with a *TH* of 0, the microphase separated structure was not distinctly observed. On the other hand, in the case of the bright field images obtained for *TH* values of 1, 3 and 48 h, the microphase separated structures of locally aligned layers were observed. *Figure 8* indicates that a non-equilibrium mixed phase at a *TH* of 0 gradually changed to the equilibrium microphase separated structure after holding on the water surface at 293 K. A PS chain in the two-dimensional ultrathin film at 293 K is frozen in a non-equilibrium state because this temperature is much lower than the T_g of PS.

Figure 9 shows the Fourier transform patterns of the bright field images shown in *Figure 8*. The Fourier transform pattern at a *TH* of 0 does not show any peak. On the other hand, the Fourier transform patterns at *TH* values of 1, 3 and 48 h showed the broad arcs

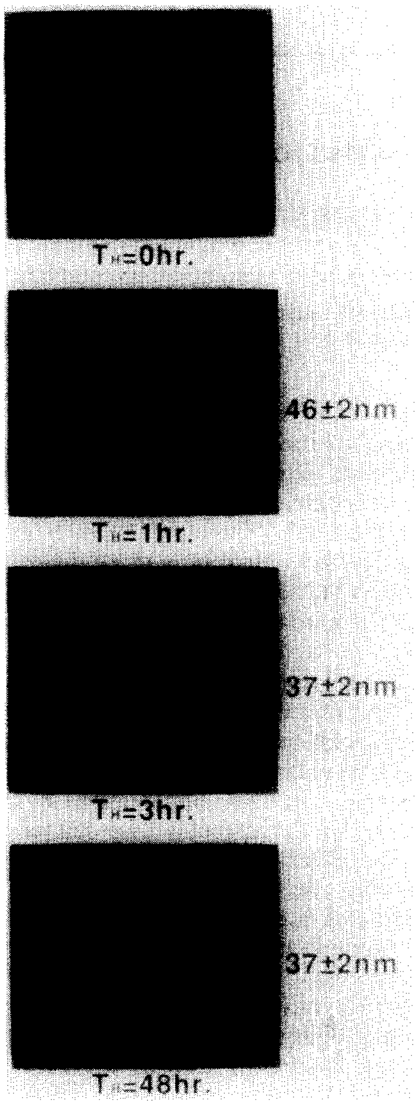

Figure 9 Fourier transform patterns of the bright field images of the two-dimensional ultrathin SBS films shown in *Figure 8*

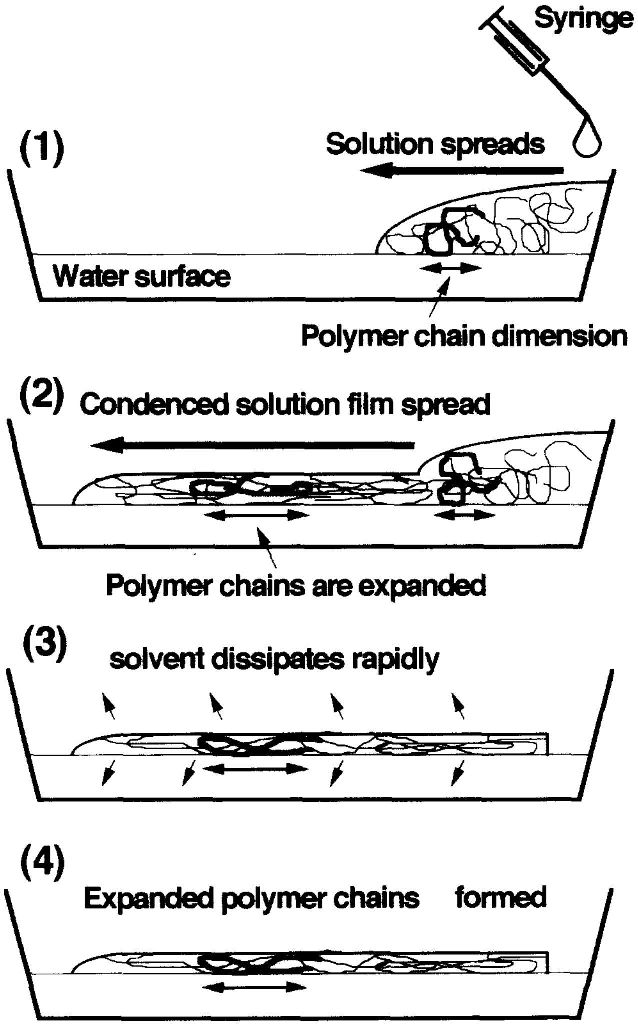

Figure 10 Schematic representation of the formation process of a two-dimensional ultrathin film by the water casting method

corresponding to the long periods of the microphase separated layered structures of SBS. The intensities of the broad arcs increased and the arcs became sharper with an increase in *TH*. Therefore, *Figure 9* indicates that the periodic layered structure is more distinctly formed with an increase in the holding time on the water surface. The structural periods estimated from the peak positions in the Fourier patterns where *TH* is 1, 3 and 48 h were 46, 37 and 37 nm, respectively, as shown on *Figure 9*. In the three-dimensional bulk stage, as prepared by the solvent casting method, the structural period was 37 nm. These results indicate that the structural period in the two-dimensional ultrathin films decreases during the microphase separation process and reaches the same period as that observed in the three-dimensional bulk state. Generally, the structural period remains almost constant, or increases slightly, owing to the non-Gaussian to Gaussian conformational change during the microphase separation process[19,20]. Therefore, the decrease of the structural period during the phase separation process of the two-dimensional ultrathin SBS film is characteristic, and thus may be mainly due to a relaxation of the expanded polymer chain to the same dimension as the polymer chain in the three-dimensional bulk state. Therefore, the relaxation of the expanded polymer chain may cause the contraction of the film dimension as shown in *Figure 7*.

From the relaxation behaviour of the two-dimensional ultrathin SBS film held on the water surface, it was confirmed that the two-dimensional ultrathin film prepared by the water casting method was in a non-equilibrium state immediately after film formation. Of course, the thermodynamic forces of the microphase separation will affect the conformation of the SBS film, so, therefore, its relaxation behaviour cannot be considered to be completely equivalent to that of the PS film. However, it is useful to recognize that the SBS film immediately after film formation was in a non-equilibrium state and that the PS film was prepared by the same water casting method. Thus, we may say that the expanded PS chain is in a non-equilibrium state and will relax to an equilibrium state if micro-Brownian motion occurs in the two-dimensional ultrathin PS film.

It is inferred that the film formation process of water casting led to formation of a non-equilibrium two-dimensional ultrathin film in which the polymer chain was expanded. A non-equilibrium state should arise from the film formation process as follows. In the case of water casting, a polymer chain is expanded or stretched owing to the rapid spreading of the solution on the water surface, after which it is then frozen in an expanded state due to the rapid dissipation of the solvent. *Figure 10* shows a schematic representation of the formation process of a two-dimensional ultrathin film by the water casting method. The film formation process consists of the following stages:

(1) solution spreading with an initial dissipation of the solvent;
(2) formation of a condensed solution layer with expanded polymer chains;
(3) rapid solvent dissipation from the condensed solution layer, due to the remarkably large surface/volume ratio;
(4) formation of the dried film in a miscible state of the PS and PB phases with the fixation of an expanded polymer chain.

The chain conformation in the two-dimensional ultrathin film is unstable owing to the small conformational entropy and the characteristic aggregation structure formed during the film formation process as described above. The conformation of the polymer chains has a tendency to change into that of the three-dimensional unperturbed Gaussian chain. Therefore, in order to use the two-dimensional ultrathin films in functional engineering applications, it must be important to stabilize the conformation of the polymer chains in the two-dimensional ultrathin film.

CONCLUSIONS

The parameter *D* representing the two-dimensionality, was defined as the ratio of the thickness of the two-dimensional state to twice the radius of gyration of the three-dimensional unperturbed Gaussian chain. On the basis of a Monte-Carlo simulation used for estimating the number of contacts between two segments of an unperturbed Gaussian chain in a two-dimensional state, the aggregation structure of the equilibrium two-dimensional ultrathin film was classified by *D*. In the region where $D > 0.3$, the excluded volume effect caused by the restricted dimension was not unexpected, since the segment density of an unperturbed Gaussian chain is comparable to that of the three-dimensional state. Therefore, the polymer chain dimension parallel to the film surface should be equal to that of an unperturbed Gaussian chain in the region where $D > 0.3$, which is equivalent to that in the three-dimensional solid state. In the region where $D \ll 0.3$, the polymer chains might have a tendency to not behave as unperturbed chains.

A PS chain in a two-dimensional ultrathin film prepared by the water casting method expanded in the direction parallel to the film surface, even in the case for $D \sim 1$. This characteristic aggregation structure should indicate that the two-dimensional ultrathin PS film prepared by the water casting method was in a non-equilibrium state.

By holding the two-dimensional ultrathin SBS film on the water surface, the following features were observed:

(1) the film dimension decreased;
(2) the homogeneous state immediately after formation of the film changed into the microphase separated state;
(3) the structural period of the microphase separation decreased.

These phenomena may be due to a relaxation of the expanded polymer chain. It was concluded that the two-dimensional ultrathin SBS film immediately after formation was in a non-equilibrium state, and then changed into a stable state.

In the two-dimensional ultrathin film prepared by the water casting method, the radius of gyration in the direction parallel to the film surface was larger than the radius of gyration of a three-dimensional unperturbed chain. This characteristic aggregation structure of the two-dimensional ultrathin film may be caused by the fixation of the polymer chain conformation in the spreading solution stage, owing to a rapid dissipation of the solvent during the water casting process. Of course, other possible causes may be found in the future. We expect that a complete theory for the aggregation structure of two-dimensional ultrathin films will eventually be developed.

REFERENCES

1 Flory, P. J. *J. Chem. Phys.* 1949, **17**, 303
2 Cotton, J. P., Decker, D., Benoit, H., Farnoux, B., Higgins, J., Jannink, G., Ober, R., Picot, C. and des Cloizeaux, J. *Macromolecules* 1974, **7**, 863
3 Hamada, F., Hayashi, H. and Nakajima, A. *J. Appl. Crystallogr.* 1979, **11**, 514
4 Cassasa, E. F. *Macromolecules*, 1976, **9**, 182
5 Dimarzio, E. A. and Rubin, R. J. *J. Chem. Phys.* 1971, **55**, 4318
6 Daoud, M. and de Gennes, P. G. *J. Phys. (Paris)* 1977, **38**, 85
7 de Gennes, P. G. *Macromolecules* 1982, **15**, 492
8 Ishinabe, T. *J. Chem. Phys.* 1985, **83**, 423
9 Shiokawa, K. *Polym. J.* 1990, **22**, 925
10 Shuto, K., Oishi, Y., Kajiyama, T. and Han, C. C. *Polym. J.* 1993, **25**, 291
11 Shuto, K., Oishi, Y., Kajiyama, T. and Han, C. C. *Macromolecules* 1993, **26**, 6589
12 Krigbaum, W. R., Kurz, J.E. and Smith, P. *J. Phys. Chem.* 1961, **65**, 1984
13 Hamamoto, A., Fuji, M., Tanaka, G. and Yamakawa, H. *Polym. J.* 1971, **2**, 799
14 de Gennes, P.G. 'Scaling Concepts in Polymer Physics', Cornell University Press, New York, 1979, p. 54
15 Ober, R. and Vilanove, R. *Colloid Polym. Sci.* 1977, **255**, 1067
16 Kumaki, J. *Macromolecules* 1986, **19**, 956
17 Mark, J. E. *J. Am. Chem. Soc.* 1967, **89**, 6829
18 Inoue, T., Soeno, T., Kawai, H., Fukatsu, M. and Kurata, M. *J. Polym. Sci.* 1968, **6**, 75
19 Bates, F. S. and Hartney, M. A. *Macromolecules* 1985, **18**, 2478
20 Russell, T. P. *Macromolecules* 1989, **22**, 3380