Effect of Polydispersity on Surface Molecular Motion of Polystyrene Films

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ABSTRACT: Surface molecular motions of monodisperse polystyrene (PS) films, their binary and ternary blend films, and commercially available polydisperse PS films were investigated on the basis of scanning force microscopic (SFM) measurements at 293 K. The monodisperse PSs were synthesized by a living anionic polymerization. The binary and the ternary PS blends were prepared by mixing monodisperse PSs with different molecular weights. The commercially available PSs were used as the polydisperse PS sample. In the case of the monodisperse PS film with number-average molecular weight, M_n, lower than ca. 30k, it was revealed that the surface was in a glass−rubber transition state even at room temperature due to excess free volume induced by the surface localization of chain end groups. SFM measurements revealed that the surfaces of the binary and the ternary PS blend films were in a glass−rubber transition state even at room temperature, when a component with M_n lower than ca. 30k existed. A more vigorous surface molecular motion for the binary and the ternary PS blend films compared with the bulk can be explained by the surface segregation of the lower molecular weight component. In the case of the polydisperse PS film, even though the molecular weight distribution was broad and the somewhat lower molecular weight component was mixed, the active surface molecular motion showing a glass−rubber transition state was remarkably depressed at room temperature in comparison with the case for the monodisperse PS film with corresponding M_ns. The difference in surface thermal molecular motion between the monodisperse and the commercial polydisperse PS films might be explained on the basis of the chemical structure of the chain end groups. Also, for the case that the lower molecular weight component was not present in the system in spite of the broad molecular weight distribution, the surface molecular motion corresponding to a glass−rubber transition state was not observed at room temperature.

Introduction

Since applications of polymeric surface functionality as permselective membranes, biomaterials, adhesives, lubricants, and so on, are closely related to its surface aggregation structure and surface molecular motions.[1,2] Studies on surface aggregation structure and surface molecular motions for polymeric solids are quite important for practical applications as well as scientific interests. Surface aggregation structure has been investigated for the last few decades, both experimentally and theoretically, and many facts have been collected.[3−6] Only a little information, however, has been obtained on the surface molecular motions of the polymeric solids.

In the case of the polymeric ultrathin film, since the ratio of air/polymer and polymer/substrate interfaces to its total volume is somewhat larger than that of the bulk sample, it can be easily predicted that the molecular motion in ultrathin films is quite different from that of the bulk sample. Molecular motions in ultrathin films have been investigated on the basis of the temperature dependence of the film thickness evaluated by ellipsometric and/or X-ray reflectivity measurements.[7−9] Jones et al. proposed the definition that the temperature at which the slope on the temperature−thickness curve starts to change is the glass transition temperature, T_g, of the ultrathin film and then revealed that the T_g of the polystyrene (PS) ultrathin film decreases with the film thickness in the case where the thickness is less than ca. 50 nm.[8] Since a liquidlike thin layer existed at the film surface, T_g decreases with the film thickness. Their conclusion indicates that surface molecular motion is fairly active compared with bulk molecular motion. On the other hand, van Zanten et al. investigated the thermal behavior of a poly(2-vinylpyridine) ultrathin film and concluded that the T_g in the thin film was higher than that in the bulk due to the presence of a layer reduced chain mobility at the polymer/solid interface.[9] Russell and a co-worker investigated the diffusion coefficient, *D*, along the direction parallel to the film surface of a polymer chain labeled with a fluorescent dye in the (PS/labeled PS) blend film on the basis of the fluorescence recovery after patterned photobleaching (FRAPP) method.[10] In the case of a film thickness less than 150 nm, it was revealed that the magnitude of *D* decreased with the film thickness. These results tell us that the presence of the air/polymer interface and the polymer/substrate one strongly affects molecular motions in the thin films.

Recently, Russell et al. investigated, by using near-edge X-ray absorption fine structure (NEXAFS), surface relaxation behavior of the higher molecular weight PS thin film.[11] As a result, complete relaxation of the surface chains was not observed below the bulk T_g and no evidence of enhanced mobility at the film surface was found. On the other hand, the authors proposed a new method to evaluate the surface T_g of the polymeric solids based on the combination of temperature- and angular-dependent X-ray photoelectron spectroscopic (TDXPS and ADXPS) measurements and obtained the depth dependence of the surface T_g for the poly(styrene-*block*-methyl methacrylate) diblock copolymer (P(St-*b*-MMA)) films.[12−13] It was revealed that the surface T_g was much lower than that for its bulk sample and, also, the surface T_g gradually increased along a deeper direction from the air/polymer interface.

The purpose of this study is to reveal the surface molecular motion of the PS solid films on the basis of

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Table 1. Characterizations of Monodisperse PS Used in This Study

M_n	M_w/M_n	T_g/K
1.7k	1.09	335.3
2.7k	1.10	341.8
4.9k	1.08	353.5
7.5k	1.09	367.1
9.0k	1.09	368.4
19.7k	1.07	364.9
26.6k	1.09	372.0
40.4k	1.08	374.5
47.5k	1.05	379.5
140k	1.06	381.5
219k	1.04	382.1
1000k[a]	1.18	380.4
1460k[b]	1.04	382.1

[a] Deuterated PS purchased from Polymer Laboratories Co., Ltd.
[b] Purchased from Polymer Laboratories Co., Ltd.

lateral force microscopic (LFM)[14,15] and scanning viscoelasticity microscopic (SVM)[16−19] observations. It is also called forced modulation scanning force microscopic measurements.[20,21] LFM can evaluate the magnitude of the lateral force between the sample surface and the sliding cantilever tip, and also, SVM can reveal the relationships between stimulation dynamic strain and response stress at the polymeric solid surface. In this study, the surface molecular motions for the monodisperse PS films, the binary and the ternary PS blend films composed of monodisperse PSs, and also the commercially available polydisperse PS films were investigated.

Experimental Section

Materials. Tables 1 and 2 show the physico-chemical properties such as number-average molecular weight, M_n, the molecular weight dispersity, M_w/M_n, where M_w is the weight-average molecular weight, and the bulk glass transition temperature, T_g, for the PS used in this study. Monodisperse PSs were prepared by a living anionic polymerization at 293 K using *sec*-butyllithium as an initiator. The binary and the ternary PS blends were prepared by mixing monodisperse PSs which were synthesized by living anionic polymerization, and also, polydisperse PSs were commercially available. All samples were reprecipitated from a toluene solution into methanol two times. The magnitudes of M_n and M_w/M_n were determined via gel permeation chromatography (GPC, Asahi Chemical Industry GSM-700 column) with polystyrene standards. Bulk T_g was evaluated on the basis of differential scanning calorimetric (DSC 8230, Rigaku Co., Ltd.) measurement at a heating rate of 10 K·min^{-1} under dry nitrogen purge. The PS films of ca. 200 nm thickness were coated from a toluene solution onto a silicon wafer with native oxide layer by a spin-coating method.

Surface Molecular Motion. In order to investigate the relaxation behaviors at the PS film surface, the LFM measurement was carried out at 293 K in air under a repulsive force of ca. 25 nN. The LFM equipment used in this study was SPA 300 (Seiko Instruments Industry Co., Ltd.) with an SPI 3700 controller. A commercially available silicon nitride (Si_3N_4) cantilever with integrated tips (Olympus Co., Ltd.) was used. The nominal spring constant of the cantilever was 0.09 N·m^{-1}. The magnitude of lateral force was evaluated by a line scan mode. The surface dynamic viscoelastic functions of the PS film were evaluated on the basis of the SVM measurement. The evaluation method of the surface viscoelastic functions was published elsewhere.[19] The SVM measurement was performed at 293 K in air under a repulsive force of ca. 25 nN. The modulation frequency and the modulation amplitude at the supporting part of the cantilever were 4 kHz and 1.0 nm, respectively. The cantilever used for the SVM measurement was the same as that for the LFM measurement.

Results and Discussion

Monodisperse PS Films. The frictional behavior of the polymeric solids is closely related to its viscoelastic properties.[22−24] Thus, it is possible to investigate the surface molecular motion of the polymeric solids by using LFM, which can detect the lateral force between the solid surface and the sliding cantilever tip on the nanometer scale. Since the scanning rate dependence of the lateral force corresponds well to the frequency dependence of loss modulus E'',[19] it can be concluded that the polymeric solid surface is in a glass−rubber transition state, in the case that the magnitude of the lateral force depends on the scanning rate. Figure 1 shows the scanning rate dependence of lateral force for the monodisperse PS film at 293 K as a function of M_n. The tip indent depth evaluated by Hertz's elastic theory[25] was ca. 1.1 nm.[19] Also, the scanning rate, ν, of the LFM measurement can be related to the frequency, f, of the SVM measurement according to Hertz's elastic theory as given by eq 1, where μ, E, R, and F_c

$$\nu = 2f\left[\frac{3}{4}\left(\frac{1-\mu_{\text{tip}}^{2}}{E_{\text{tip}}} + \frac{1-\mu_{\text{polymer}}^{2}}{E_{\text{polymer}}}\right)RF_c\right]^{1/3} \qquad (1)$$

are the Poisson ratio, the modulus, the radius of curvature of the tip, and the contact force, respectively. The broken arrows in Figure 1 denote the scanning rates corresponding to the frequency of SVM measurements, which were calculated from eq 1. Since the distinct scanning rate dependence of lateral force was not observed in the case of M_n of 140k, it seems reasonable to consider that the surface is in a glassy state at 293 K. On the other hand, the magnitudes of surface lateral force for the monodisperse PS films with M_n less than 40.4k were apparently dependent on the scanning rate. In the case of M_n of 40.4k, although the scanning rate dependence of the lateral force was not observed in a high scanning rate region, the lateral force increased with a decrease in the scanning rate in a low scanning rate region. This result then apparently indicates that the surface of the monodisperse PS film with M_n of 40.4k is clearly in a glass−rubber transition state and in a glassy one in low and high scanning rate regions at 293 K, respectively. In the case of M_ns of 26.6k and 19.7k, since the lateral force continuously increased with a decrease in the scanning rate, it can be concluded that the surface is in a glass−rubber transition state at 293 K. Moreover, in the case of M_n of 9.0k and 4.9k, a peak was clearly observed on the lateral force−scanning rate curve. This indicates that the magnitude of surface E'' might exhibit a maximum at the corresponding frequency range to the scan-

Table 2. Characterizations of Polydisperse PS Used in This Study

sample	M_n	M_w/M_n	T_g/K	remarks
binary 1	370k	3.49	377.9	(PS19.7k/dPS1000k) (5/95 w/w)
binary 2	36k	2.52	376.8	(PS19.7k/PS140k) (50/50 w/w)
binary 3	166k	1.19	381.6	(PS140k/PS219k) (50/50 w/w)
ternary	65k	7.17	379.6	(PS19.7k/PS219k/PS1460k) (25/50/25 w/w/w)
polydisperse 1	29k	6.26	375.5	HF11
polydisperse 2	169k	2.67	377.8	US305

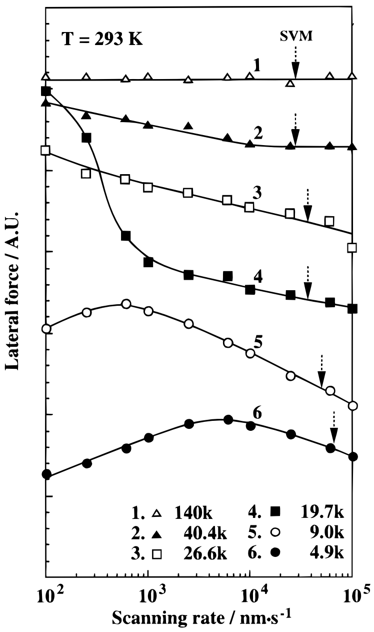

Figure 1. Scanning rate dependence of lateral force for the monodisperse PS films as a function of M_n at 293 K. The broken arrows in the Figure denote the scanning rate corresponding to the frequency of SVM measurement.

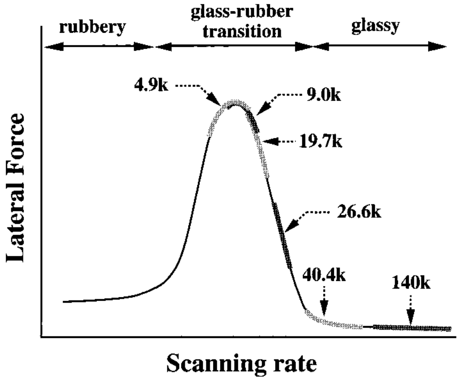

Figure 2. Schematic representation of the scanning rate−lateral force curve for the monodisperse PS film.

ning rate employed in this study. That is, the surface of the monodisperse PS film with M_n of 9.0k and 4.9k is in a glass−rubber transition state even at 293 K, even though the bulk T_g is around 360 K as shown in Table 1. Since the surface T_g for the monodisperse PS film with M_n of 9.0k is higher than that for M_n of 4.9k, it is reasonable that the peak on the lateral force−scanning rate curve for the monodisperse PS film with M_n of 9.0k appears in a lower scanning rate region in comparison with that for M_n of 4.9k. Although the annealing treatment of the monodisperse PS film was carried out at 393 K for 24 h in order to confirm the effect of the relaxation of a nonequilibrium state on lateral force, no distinct change in the lateral force was observed. Figure 2 shows the schematic representation of the scanning rate dependence of lateral force for the monodisperse PS films with different M_n at 293 K.

In order to evaluate surface storage modulus, E', and surface loss tangent, tan δ, the SVM measurements for the monodisperse PS films were carried out at 293 K in air. The method used to evaluate surface viscoelastic functions by SVM has been published elsewhere.[19] Figure 3 shows the molecular weight dependence of surface E' and surface tan δ for the monodisperse PS films. The magnitudes of bulk tan δ and bulk T_g shown in Figure 3b were evaluated by using Rheovibron (DDV-01FP, Orientec Co., Ltd.) and DSC, respectively. In a M_n range larger than 40.4k, the magnitudes of surface E' and surface tan δ were almost constan, and their magnitudes were ca. 4.5 GPa and 0.01, respectively. Then, it seems reasonable to conclude from the magnitudes of surface E' and surface tan δ that the surface is in a glassy state at 293 K for the monodisperse PS film with M_n larger than 40.4k. The LFM measurement revealed, however, that the film surface with M_n of 40.4k was in a glass−rubber transition state and a glassy one in low and high scanning rate regions, respectively, as shown in Figure 1. Since the SVM measuring frequency of 4 kHz corresponds to the LFM scanning rate of 2.7×104 nm·s^{-1} as calculated by using eq 1, it is reasonable that the film surface is in a glassy state in the case of the SVM measurement. In the case of M_n smaller than 26.6k, the magnitudes of surface E' and surface tan δ decreased and increased with a decrease in M_n, respectively, as shown in Figure 3. The magnitudes of surface E' and surface tan δ indicate that the surface of the monodisperse PS film with M_n smaller than 26.6k is in a glass−rubber transition state even at 293 K. The bulk dynamic viscoelastic properties of the monodisperse PS samples were measured in order to compare with the surface dynamic viscoelastic ones. Since the film was very fragile in the case of M_n smaller than 40.4k, a dynamic spring analysis technique was applied to evaluate the magnitude of bulk tan δ. In the case of M_n smaller than 26.6k, the magnitude of surface tan δ was much higher than that of bulk tan δ as shown in Figure 3b. Since the bulk T_g generally corresponds to the temperature at the initial increase point on the tan δ−temperature curve, this clearly indicates that the surface T_g of the monodisperse PS film is more strongly dependent on M_n than the bulk one. Also, the bulk T_g for the monodisperse PS evaluated by DSC was much higher than 293 K in all M_n ranges. Thus, it seems reasonable to conclude that the thermal molecular motion at the film surface for the monodisperse PS is more activated in comparison with that for the bulk sample at 293 K, especially in the case of M_n smaller than 26.6k.

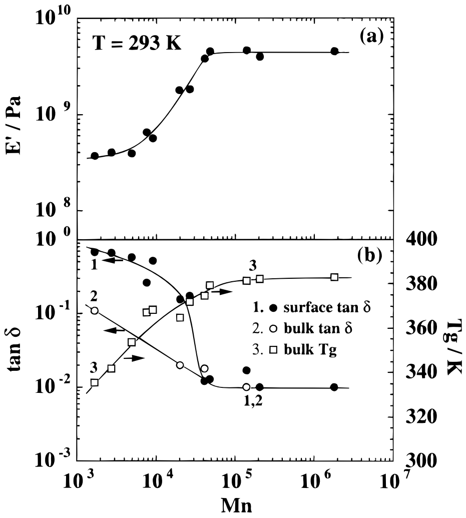

Figure 3. Molecular weight dependence of (a) surface E' and (b) surface tan δ for the monodisperse PS films at 293 K. Also, bulk tan δ and bulk T_g are present in part b.

A remarkable lowering of the surface T_g compared with bulk one can be explained by a surface excess free volume due to the surface localization of chain end

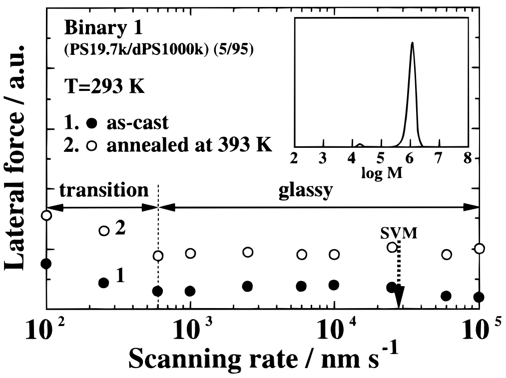

Figure 4. Scanning rate dependence of lateral force for the binary 1 film at 293 K. The filled and the open circles denote the lateral force for the as-cast binary 1 film and one annealed at 393 K for 24 h, respectively. The inset in the figure shows the molecular weight distribution of the binary 1 system evaluated by GPC measurement. The broken arrow in the figure shows the scanning rate corresponding to the frequency of SVM measurement.

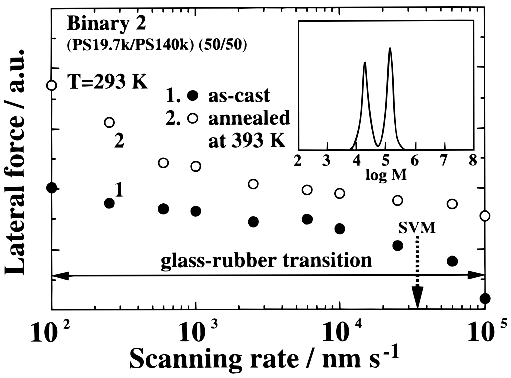

Figure 5. Scanning rate dependence of lateral force for the binary 2 film at 293 K. The filled and the open circles denote the lateral force for the as-cast binary 2 film and the one annealed at 393 K for 24 h, respectively. The inset in the figure shows the molecular weight distribution of the binary 2 system. The broken arrow in the figure shows the scanning rate corresponding to the frequency of SVM measurement.

groups.[13,17−19,26] When the chain end groups are preferentially localized at the film surface, an excess free volume was induced at the film surface due to a larger freedom of chain end groups compared with main chains.

Binary PS Blend Films. Surface molecular motion, that is, the scanning rate dependence of lateral force for the binary and the ternary PS blends as a model for the polydisperse PS, has been investigated. Figure 4 shows the scanning rate dependence of lateral force for the binary 1 film at 293 K. The binary 1 film was prepared by mixing monodisperse PSs with M_n of 19.7k and deuterated PS (dPS) with M_n of 1×10^6. The blend ratio of (PS/dPS) was (5/95) in weight. The filled and the open circles correspond to the lateral force for the as-cast binary 1 film and the one annealed at 393 K for 24 h, respectively. The inset in Figure 4 shows the molecular weight distribution of the binary 1 system, evaluated by GPC measurement. Also, the broken allow shows the scanning rate corresponding to the frequency of the SVM measurement. Both films did not exhibit the distinct scanning rate dependence of lateral force at a scanning rate range higher than 6×10^2 nm·s^{-1}. On the other hand, the magnitude of the lateral force increased with a decrease in the scanning rate in a scanning rate region lower than 6×10^2 nm·s^{-1}. Then, Figure 4 indicates that the surface is in a glass−rubber transition state and in a glassy one in lower and higher scanning rate regions, respectively, even at 293 K. The magnitudes of surface E' and surface tan δ for the as-cast binary 1 film evaluated by the SVM measurement at 293 K were 4.3 GPa and 0.02. This clearly shows that the surface is in a glassy state at the scanning rate corresponding to the SVM measurement. On the basis of the result of Figure 1, it is reasonable to consider that the scanning rate dependence of lateral force for the binary 1 film might arise from the monodisperse PS component with M_n of 19.7k.

In order to confirm the surface molecular motion−structure relationship for the binary 1 film mentioned above, a DSIMS measurement was carried out.[17] The proton and deuterium ion intensities apparently increased and decreased at the air/polymer interface. Since only the lower molecular weight component, that is PS with M_n of 19.7k, was protonated, it can be concluded that the lower molecular weight component was preferentially segregated at the air/polymer interface.[27] It should be noted that the lower molecular weight component was enriched at the film surface in spite of the higher surface free energy component due to the larger polarizability of the C−H bond compared with that of the C−D bond.[28] The surface segregation of the lower molecular weight component can be explained on the basis of two factors: the surface localization of chain end groups and the conformational entropy loss of the chain being present at the film surface. A more detailed explanation of the surface enrichment of the lower molecular weight component with higher surface free energy will be given elsewhere.[29] Since the concentration of the chain end groups is proportional to $2/N$, where N is the degree of polymerization, the surface segregation of the lower molecular weight component induces an excess free volume at the film surface, resulting in greater activated surface molecular motion in comparison with that of the higher molecular weight component. Thus, it seems reasonable to conclude that the surface of the binary 1 film is in a glass−rubber transition state even at 293 K due to the surface localization of the lower molecular weight component at the lower scanning rate range, in spite of the fact that bulk T_g is 378 K.

Figure 5 shows the scanning rate dependence of lateral force for the binary 2 film at 293 K. The binary 2 film was prepared by mixing monodisperse PSs with M_ns of 19.7k and 140k with a blend ratio of (50/50) in weight. The filled and the open circles show the lateral force for the as-cast binary 2 film and the one annealed at 393 K for 24 h, respectively. The inset in Figure 5 shows the molecular weight distribution of the binary 2 system evaluated by GPC measurement. Lateral force of the as-cast binary 2 film increased with a decrease in the scanning rate in all scanning rate region studied here. The magnitudes of surface E' and surface tan δ evaluated by SVM measurement at 293 K were 2.3 GPa and 0.05, respectively. These LFM and SVM results indicate that the surface of the as-cast binary 2 film is in a glass−rubber transition state even at 293 K. Since the magnitudes of surface E' and surface tan δ for the monodisperse PS film with M_n of 19.7k were 1.8 GPa and 0.15, respectively, as shown in Figure 3, it appears that the PS with M_n of 19.7k is preferentially segregated at the film surface. When the binary 2 film was annealed at 393 K for 24 h, the scanning rate dependence of the lateral force became more pronounced than that for the as-cast one. Its scanning rate−lateral force

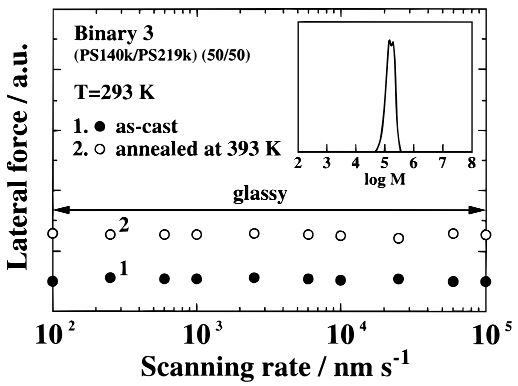

Figure 6. Scanning rate dependence of lateral force for the binary 3 film at 293 K. The filled and the open circles denote the lateral force for the as-cast binary 3 film and the one annealed at 393 K for 24 h, respectively. The inset in the figure shows the molecular weight distribution of the binary 3 system.

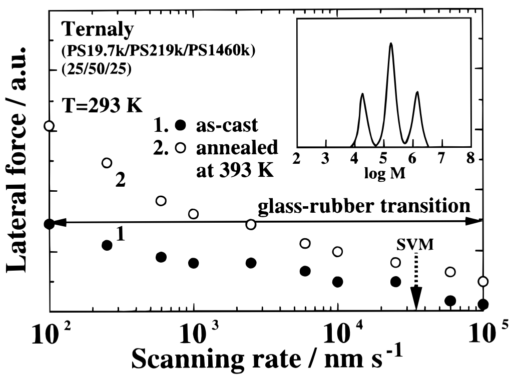

Figure 7. Scanning rate dependence of lateral force for the ternary film at 293 K. The filled and the open circles denote the lateral force for the as-cast ternary film and the one annealed at 393 K for 24 h, respectively. The inset in Figure shows the molecular weight distribution of the ternary PS blend. The broken arrow in the figure shows the scanning rate corresponding to the frequency of SVM measurement.

curve is fairly similar to that for the monodisperse PS film with M_n of 19.7k as shown in Figure 1. Then, it seems reasonable to conclude that the surface enrichment of PS with M_n of 19.7k becomes prominent by annealing the binary 2 film at 393 K for 24 h, and then, the surface molecular motion is more activated than that of the as-cast binary 2 film.

Figure 6 shows the relationship between the scanning rate and lateral force for the binary 3 film at 293 K. The binary 3 system was prepared by mixing monodisperse PSs with M_ns of 140k and 219k with the blend ratio of (50/50) in weight and, thus, did not include any component of which surface was in a glass−rubber transition state at room temperature. The filled and the open circles show the lateral force for the as-cast binary 3 film and the one annealed at 393 K for 24 h, respectively. The inset in Figure 6 shows the molecular weight distribution of the binary 3 system evaluated by GPC measurement. The lateral force of both the as-cast binary 3 film and the one annealed was not dependent on the scanning rate in the entire scanning rate region employed in this study. This result indicates that the surface of the binary 3 film is in a glassy state at room temperature. Thus, it can be concluded on the basis of the SFM results for the binary 1, 2, and 3 films that the surface molecular motion is not activated at room temperature, if the component with M_n lower than ca. 30k does not exist in the system.

Ternary PS Blend Film. The investigation of the surface molecular motion has been extended to the ternary PS blend system. Figure 7 shows the scanning rate dependence of lateral force for the ternary film at 293 K. The ternary PS blend system was composed of monodisperse PSs with M_ns of 19.7k, 219k, and 1460k with blend ratio of (25/50/25) in weight. The filled and the open circles show the lateral force for the as-cast ternary film and the one annealed at 393 K for 24 h, respectively. Since the as-cast ternary film and the one annealed showed a distinct scanning rate dependence of the lateral force, it seems reasonable to conclude that surface molecular motion is fairly activated in comparison with the bulk one due to the preferential surface segregation of PS with M_n of 19.7k. Since annealing of the film induces more extensive surface localization of PS with smaller M_n, the scanning rate dependence of lateral force for the one annealed became more pronounced in a similar fashion to the binary blend film. The magnitudes of surface E' and surface tan δ for the ternary 1 film at 293 K were 2.3 GPa and 0.07, respectively. Therefore, the SVM measurement also exhibited the surface in a glass−rubber transition state.

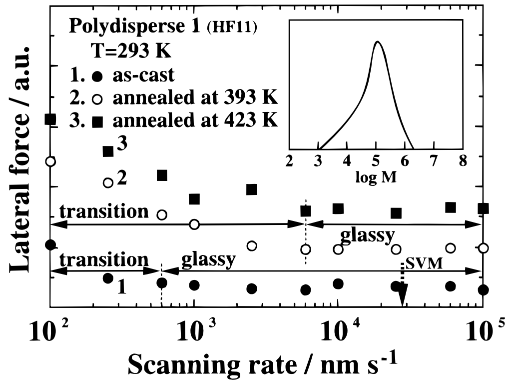

Figure 8. Scanning rate dependence of lateral force for the polydisperse 1 film at 293 K. The filled circles, the open circles, and the filled squares denote the lateral force for the as-cast polydisperse 1 film and the ones annealed at 393 and 423 K for 24 h, respectively. The inset in the figure shows the molecular weight distribution of the polydisperse 1 system. The broken arrow in the figure shows the scanning rate corresponding to the frequency of SVM measurement.

Polydisperse PS Films. Figure 8 shows the scanning rate dependence of lateral force for the commercially available polydisperse 1 film at 293 K. The filled circles, the open circles, and the filled squares show the results for the as-cast polydisperse 1 film and the ones annealed at 393 and 423 K for 24 h, respectively. In the case of the as-cast polydisperse 1 film, the scanning rate dependence of lateral force was not apparent at higher scanning rate than 6×10^2 nm·s^{-1}, and the lateral force slightly increased with a decrease in the scanning rate at a scanning rate lower than 6×10^2 nm·s^{-1}. This indicates that, in the lower scanning rate region, the surface is in a glass−rubber transition region even at 293 K. The magnitudes of surface E' and surface tan δ for the as-cast polydisperse 1 film evaluated by SVM measurement at 293 K were 4.4 GPa and 0.02, respectively, indicating a glassy state at a corresponding scanning rate shown by the broken arrow. When the annealing treatment of the polydisperse 1 film was carried out at 393 and 423 K for 24 h, the scanning rate dependence of lateral force became more distinct up to 2.5×10^3 nm·s^{-1}. However, the scanning rate−lateral force curves are very similar for the two annealed

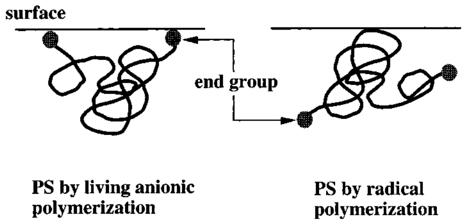

Figure 9. Schematic illustration of the molecular aggregation state for PSs prepared by living anionic and radical polymerizations at the film surface.

films. These results indicate that when the annealing treatment of the polydisperse 1 film was performed, the lower molecular weight component was preferentially segregated at the film surface and, also, the annealing effect was almost the same in the case of annealing above bulk T_g. The polydisperse 1 system has a broad molecular weight distribution and contains a much lower molecular weight component as shown by the inset in Figure 8. Even though a fairly high fraction of the lower molecular weight component with M_n lower than ca. 30k was contained in the polydisperse 1 system, the scanning rate dependence of lateral force corresponding to a glass−rubber transition state was not distinct in comparison with that for the monodisperse PS film with M_n smaller than ca. 30k as shown in Figure 1. This difference might be explained on the basis of the chemical structure of chain end groups as shown in Figure 9.

Figure 9 shows the schematic representation of the molecular aggregation state of a polymeric chain at the air/polymer interface for PSs prepared by living anionic and radical polymerizations. If chain end group has a lower surface free energy compared with the main chain part, the chain end group is preferentially localized at the film surface.[30] In the case of the PS prepared by living anionic polymerization using *sec*-butyllithium as an initiator, the two chain end groups are the butyl group and the repeating unit, respectively. In this case, since the magnitudes of the surface free energy for the chain end groups are smaller than that of the main chain,[31] chain end groups are preferentially segregated at the film surface.[17−19] However, in the case of the PS prepared by radical polymerization using azobisisobutyronitrile, redox initiator, and so on, the hydrophilic fragments of initiator are incorporated into the chain ends because the polymerization reaction is terminated completely by recombination. Then, since the chain end group has a higher surface free energy in comparison with the main chain part, the chain end groups might be caused to migrate into a deeper surface region from the air/polymer interface.[30] Even if the lower molecular weight component is preferentially segregated at the film surface in the case of the PS prepared by radical polymerization, the end group concentration at the film surface is not increased effectively. Therefore, it seems reasonable to conclude that, in the case of the polydisperse PS prepared by radical polymerization, the remarkable activation of the surface molecular motion induced by the surface segregation of chain end groups as measured for the monodisperse PS film with smaller M_n is not apparently detected due to the preferential migration of chain end groups into a deeper surface region from the air/polymer interface.

The polydisperse 1 film contains an oligomer-like shorter chain component with M_n less than 1.5k, of which the radius of gyration of an unperturbed chain is comparable with and/or less than ca. 1 nm, as shown by the inset in Figure 8. When the load of ca. 25 nN was applied to the cantilever tip, the indentation depth of the tip calculated from Hertz' elastic theory, is ca. 1.1 nm.[19] Thus, the oligomer-like lower molecular weight component existing at the surface can be easily removed by the sliding tip. Therefore, even though the chain end groups do not segregate at the surface, the surface molecular motion is slightly activated if the oligomer-like lower M_n component is enriched at the surface.

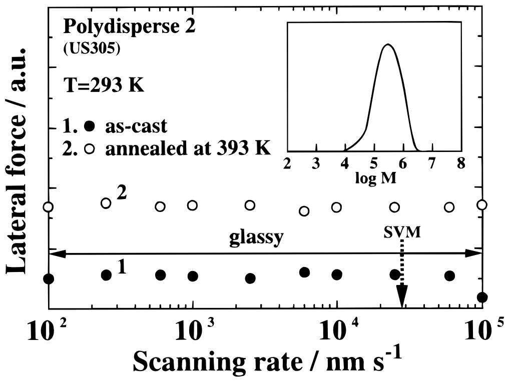

Figure 10. Scanning rate dependence of lateral force for the polydisperse 2 film at 293 K. The filled and the open circles denote the lateral force for the as-cast polydisperse 2 film and the one annealed at 393 K for 24 h, respectively. The inset in the figure shows the molecular weight distribution of the polydisperse 2 system. The broken arrow in the figure shows the scanning rate corresponding to the frequency of SVM measurement.

Figure 10 shows the scanning rate dependence of lateral force for the polydisperse 2 film at 293 K. The filled and the open circles show the lateral force for the as-cast polydisperse 2 film and the one annealed at 393 K for 24 h, respectively. In both cases, any distinct scanning rate dependence of the lateral force was not observed, because the fraction of the lower molecular weight component with M_n smaller than 30k is very low. Also, the magnitudes of surface E' and surface tan δ for the as-cast polydisperse 2 film based on SVM measurement at 293 K were 4.3 GPa and 0.02, respectively. The LFM and SVM measurements indicate that the surface of the polydisperse 2 film is in a glassy state at 293 K. Then, it can be concluded that if the fraction of the lower molecular weight component than 30k is very small in spite of the broader molecular weight distribution, the surface molecular motion is not activated at room temperature due to the negligible surface localization of chain end groups.

Conclusion

LFM and SVM measurements for the monodisperse PS films, the binary and the ternary PS blend films, and the polydisperse PS films were performed at 293 K in order to investigate the surface molecular motion. It was revealed that the monodisperse PS film surface with M_n less than ca. 30k was in a glass−rubber transition state even at 293 K due to excess free volume at the air/polymer interface induced by the surface segregation of chain end groups. In the case of the binary and the ternary PS films, which are composed of PS with M_n of 19.7k and higher molecular weight PS, it was revealed that the surface was in a glass−rubber transition state at 293 K due to the surface segregation of the lower molecular weight component, PS, with M_n of 19.7k. In the case of the polydisperse PS film, although the surface molecular motion was activated in comparison with the bulk one, the surface dynamic viscoelastic variations being characteristic of a glass–rubber transition state were not observed at 293 K in a fashion similar to that for the monodisperse PS film with M_n less than ca. 30k. The difference in the activation for the surface molecular motion between the monodisperse and the polydisperse PS films can be explained on the basis of the chemical structure of the chain end groups. Also, in the case of the broad molecular weight distribution, if there were not a lower molecular weight component, the surface molecular motion was not apparently activated at 293 K.

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