Macromolecules **2002,** *35,* 4702−4706

A Novel Method To Examine Surface Composition in Mixtures of Chemically Identical Two Polymers with Different Molecular Weights

Keiji Tanaka and Tisato Kajiyama*

Department of Applied Chemistry, Faculty of Engineering, Kyushu University, Fukuoka 812-8581, Japan

Atsushi Takahara

Institute for Fundamental Research of Organic Chemistry, Kyushu University, Fukuoka 812-8581, Japan

Seiji Tasaki

Research Reactor Institute, Kyoto University, Kumatori-cho, Sennan-gun, Osaka 590-0494, Japan

Received November 12, 2001

ABSTRACT: The bulk glass transition temperature, T_g^b, of miscible binary blends can be well expressed by the Gordon−Taylor equation. Extending this notion to surface, the surface composition in the blend would be obtained by measuring the surface glass transition temperature, T_g^s, of each constituent as well as their blend. The most intriguing advantage of this technique is that labeling of a component is not necessary, unlike conventional spectroscopy. To confirm the validity of our technique, the surface composition in a mixture of polystyrene (PS) and deuterated PS (dPS) was evaluated and compared with the results by well-established surface characterization techniques, static secondary ion mass spectroscopy, and neutron reflectivity. They were in good accordance with one another within the experimental accuracy. Hence, it was claimed that the proposed method was powerful to study the surface concentration in miscible binary blends. Finally, the surface composition in blend films of two PSs with different molecular weights was experimentally and systematically elucidated. The surface enrichment of a smaller molecular weight component became more remarkable with increasing molecular weight disparity between the two components due to an entropic effect.

Introduction

In general, synthetic polymers have a broad molecular weight distribution, and the surface of a film prepared by them would be covered with smaller molecular weight components. Hence, to design highly surface-functionalized materials such as lubricants, adhesives, and biomaterials, using synthetic polymers, it is of pivotal importance to elucidate an effect of shorter chains on aggregation states and physical properties at the surface.

One of the easier ways to study experimentally such an effect is to adopt a model blend system composed of two monodisperse polymers with different molecular weights, namely, a polymer with bimodal molecular weight distribution. To date, we have studied on surface relaxation behavior of polystyrene (PS) films with bimodal molecular weight.[1] Surface relaxation of the film was strongly dominated by the smaller molecular weight component rather than the higher one. Although it was clear that the smaller molecular weight component was preferentially partitioned to the surface, it was impossible only from this experiment to deduce to what extent the shorter component is present at the surface.

Either component must be labeled with deuterium to confer a contrast between constituents so that the surface composition of the (PS/PS) blends can be examined. Then, the surface composition of the blend of PS and deuterated PS (dPS) can be easily obtained by many established techniques, e.g., static and dynamic secondary ion mass spectrometry (SSIMS[2] and DSIMS[3,4]), forward recoil spectrometry (FRES),[4,5] nuclear reaction analysis (NRA),[6] surface-enhanced Raman spectroscopy (SERS),[7] and neutron reflectivity (NR).[3] However, it should be always kept in mind that deuterium labeling of a component makes its surface energy lower. For instance, in the case of a symmetric (PS/dPS) blend, dPS is enriched at the surface,[2−7] indicating that the surface in the (PS/dPS) blend thermodynamically differs from that in the (PS/PS) one. Hence, as long as deuterium labeling of a component is applied, the effect of molecular weight disparity on surface segregation in polymer films will not be understood in a real sense.

The objective of this study is to propose an experimental technique to study the surface composition in mixtures of chemically identical two polymers based on our surface glass transition temperature, T_g^s, measurements,[8,9] which do not need any labeling procedures. As such a system, two PSs with different molecular weights are mixed here to prepare films. A similar experiment has been conducted by Pu et al. using a shear modulation force microscope.[10]

Experimental Section

PSs with the number-average molecular weight, M_n, of 3.5K, 4.9K, 7.5K, 13K, 19.7K, 29.9K, 90K, and 140K were synthesized by a living anionic polymerization using *sec*-butyllithium as an initiator and methanol as a terminator. Their polydispersity indexes, M_w/M_n, were 1.06, 1.08, 1.09, 1.06, 1.07, 1.08, 1.09, and 1.06, respectively. Also, monodisperse PSs with M_n of 981K and 1.46 M and monodisperse dPS with M_n of 847K were purchased from Polymer Laboratories Co, Ltd. Blend

---

* To whom correspondence should be addressed: FAX +81-92-651-5606; Tel +81-92-642-3558; e-mail kajiyama@cstf.kyushu-u.ac.jp.

10.1021/ma011960o CCC: $22.00 © 2002 American Chemical Society
Published on Web 05/03/2002

films were spun-coated from toluene solutions onto cleaned silicon wafers with native oxide layer. The films were dried at 296 K for more than 24 h and then annealed at 423 K for, at least, 48 h under vacuum. Each film thickness evaluated by ellipsometric measurement was approximately 200 nm or more thick.

T_g^s of homo and blend films was determined on the basis of surface relaxation behavior using lateral force microscopy (LFM, SPA 300 HV, Seiko Instruments Industry Co., Ltd.) with an SPI 3800 controller. LFM measurement was carried out at various temperatures in vacuo so as to avoid the surface oxidation and a capillary force effect induced by surface-adsorbed water. The sample was heated with a heater located under the sample stage, and the surface temperature lower than room temperature (RT) was achieved by using liquid nitrogen. A piezoscanner was thermally insulated from the heating stage. The temperature calibration was carried out on the basis of the melting behavior of In and Ga on the sample stage, which was observed by a CCD camera. In or Ga was tightly fixed on the stage with the aid of Ag foil to attain a better thermal conductivity, and a thermocouple was precisely sandwiched between them. And then, the thermocouple was calibrated on the basis of the melting temperatures of In and Ga. In LFM measurements, a sample was similarly fixed by the Ag foil, and the temperature of the sample surface was always monitored by the thermocouple, which was sandwiched between the foil and the sample surface, during the measurement. A cantilever with a bending spring constant of 0.11 ± 0.02 N m^{-1}, of which both sides were uncoated or coated by gold, was used. The applied force to the cantilever was set to be 10 nN in a repulsive force region. Also, the bulk glass transition temperature, T_g^b, of the homo and blend samples was measured by differential scanning calorimetry (DSC8230, Rigaku Co., Ltd.). The specimen was heated to 423 K at a heating rate of 10 K min^{-1} under dried nitrogen purge.

The surface composition in mixture films composed of PS and dPS was examined by SSIMS and NR. For SSIMS measurements, Phi TRIFT II with a time-of-flight mass spectrometer was used. The sample surface with an area of 100 × 100 μm^2 was irradiated by a Ga pulse beam of 15 k eV with a current of 600 pA. The pulse width was 13 ns and was generated 10^4 times/s. The spectra integration was allowed for 3 min. NR measurements were performed using the multilayer interferometer for neutrons (C3-1-2, MINE) at the Institute for Solid State Physics, the University of Tokyo. The incident neutrons have a long wavelength of 1.26 nm and a resolution of 5.1%. The reflectivity was calculated on the basis of the scattering length density profile along the depth direction by using Spreadsheet Environmental Reflectivity Fitting.[11]

Results and Discussion

In this study, the surface composition of blend films of two PSs with different molecular weights is studied on the basis of Gordon−Taylor equation[12] assumed to be effective even at the surface. In general, T_g^b of a miscible binary polymer mixture is well expressed by T_g^b of each constituent and its volume fraction as follows:

$$T^b_{g,mix} = \frac{(KT^b_{g,1} - T^b_{g,2})\phi_1 + T^b_{g,2}}{1 + (K-1)\phi_1} \qquad (1)$$

Here, the subscript denotes each constituent, ϕ is the volume fraction, and K is the ratio of thermal expansion coefficients of the free volume, α, for both components, namely, α_1/α_2. Equation 1 is basically based on the additivity rule of the free volume and is widely accepted as the Gordon−Taylor equation.[12] Although the free volume of a component at the surface would not be the same as that in the interior bulk region, such a situation is common for both components. Hence, invoking that the additivity rule of the free volume is held at the surface, the Gordon−Taylor equation is applied to T_g^s. Since we are able to examine T_g^s of the blend film as well as each homo film,[8,9] the surface composition in the blend composed of two PSs with different molecular weights, PS1 and PS2, can be characterized by eq 2.

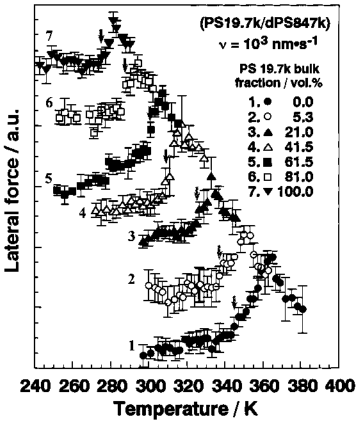

Figure 1. Lateral force−temperature curves for (PS19.7K/dPS847K) blend films with various compositions at the scanning rate of 10^3 nm s^{-1}.

$$\phi_1 = \frac{T^s_{g,mix} - T^s_{g,2}}{T^s_{g,mix} - T^s_{g,2} + K(T^s_{g,1} - T^s_{g,mix})} \qquad (2)$$

At first, to confirm the validity of the aforementioned method, the surface composition of the blend film composed of PS with M_n of 19.7K and dPS with M_n of 847K was examined. In this blend system, the surface composition can be also obtained by the well-established techniques, SSIMS and NR, because one of constituents is deuterated. This blend was completely miscible at the range of room temperature to annealing temperature of 423 K.[13] Figure 1 shows the temperature dependence of lateral force at the scanning rate of 10^3 nm s^{-1} for the (PS19.7K/dPS847K) blend films with various bulk blend ratios. Since lateral force is originated from energy dissipation during a tip slides on the sample surface, the temperature dependence of lateral force corresponds well to the dynamic loss modulus variation with temperature. A peak observed on the temperature−lateral force curves is assigned to the α_a absorption corresponding to the micro-Brownian motion of polymeric chains.[8,14] Hence, an onset temperature on the curve, that is, the temperature at which lateral force starts to increase, can be empirically defined as T_g^s,[8] as marked by arrows in Figure 1. T_g^s of the PS19.7K and dPS847K films were evaluated to be 279 and 347 K, respectively, and T_g^s values of their mixtures were dependent on the blend ratio.

Figure 2 shows T_g^b and T_g^s of the (PS19.7K/dPS847K) films with various blend compositions. The dotted lines denote the additivity rule of the glass transition temperature for bulk and surface. T_g^b of the blend linearly decreased with increasing PS19.7K fraction in the blend. This implies that the K value in the Gordon−Taylor equation can be regarded to be 1. In contrast, the relation between T_g^s and blend ratio was not linear but negatively deviated, as shown in Figure 2. This is because the abscissa is expressed by the bulk blend ratio, although PS19.7K is preferentially segregated at the blend surface. Since the value of K in eq 2 is 1, the

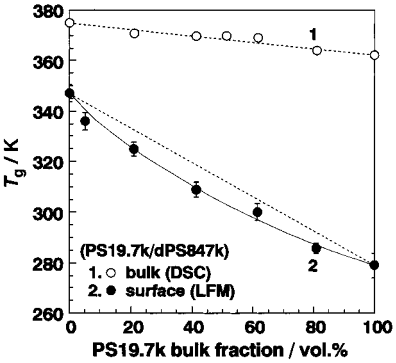

Figure 2. Bulk blend ratio dependences of T_g^b by DSC and T_g^s by LFM. Each dot line denotes a simple additivity rule of T_g. The solid curve for T_g^s is drawn to guide the eye.

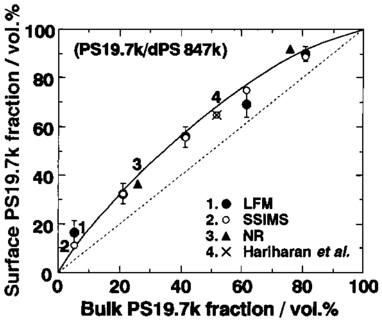

Figure 3. Relation of surface hPS fraction to bulk composition in (PS19.7K/dPS847K) blend films. Surface composition was examined by three different techniques: LFM, SSIMS, NR. The data point by Hariharan et al. using NR was adopted from Table 1 in ref 16. The broken line denotes the case where the surface and bulk compositions are the same. The solid curve is drawn to guide the eye.

surface composition in the (PS19.7K/dPS847K) blend films can be given by

$$\phi_1 = \frac{T^{s}_{g,2} - T^{s}_{g,\mathrm{mix}}}{T^{s}_{g,2} - T^{s}_{g,1}} \tag{3}$$

Figure 3 shows the bulk vs surface fraction of the PS19.7K in the (PS19.7K/dPS847K) blend films based on the T_g^s measurements by LFM. The surface fraction of PS19.7K was higher than the bulk one at all blend ratios employed. In general, the surface of (PS/dPS) blends, in which both components have the comparable high M_n, is covered with dPS owing to its lower surface energy. However, PS19.7K, which was the lower M_n component, was enriched at the blend surface in this study. This result can be understood by considering a situation where the hPS19.7K suffers less of the conformational entropic penalty at the surface in comparison with dPS847K.

Deferring the discussion of the surface segregation due to molecular weight disparity, the surface composition in the blends based on the T_g^s measurement is compared with those obtained by SSIMS and NR. Figure 4 shows a typical SSIMS spectrum of the (PS19.7K/dPS847K) film with the bulk composition of (41.5/58.5) in volume. The intense peaks observed at the mass of 91.05 and 98.10 Da can be assigned to tropylium ion, $C_7H_7^+$, and its deuterated species, $C_7D_7^+$, respectively. Also, the peaks at 92.06 and 97.09 Da are due probably to $C_7DH_6^+$ or $C_6C^{13}H_7^+$ and $C_7D_6H^+$. While the secondary ion intensities at 91.05 and 98.10 Da monotonically increased and decreased with increasing feed fraction of PS into the blend, respectively, those at 92.06 and 97.09 Da were not necessarily proportional to the blend ratio. Hence, the surface PS fraction in the blend was estimated from the value of $I_{91}/(I_{91} + I_{98})$, where I_i is the secondary ion intensity at i Da, provided that a contribution of chain end fragments to I_{91} was corrected by following the procedure of Vanden Eynde et al.[15] Also, the $(I_{91} + I_{98})/(I_{91} + I_{92} + I_{97} + I_{98})$ value was in accordance with the value of $I_{91}/(I_{91} + I_{98})$ within 5%. The surface PS fraction in the (PS19.7K/dPS847K) blend films so obtained was plotted in Figure 3.

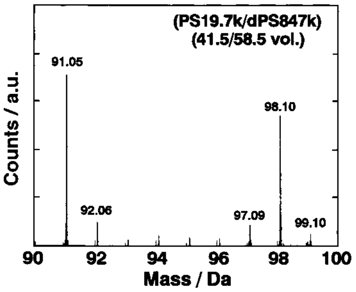

Figure 4. Positive secondary ion time-of-flight mass spectrum of (PS19.7K/dPS847K) blend film with the bulk PS fraction of 41.5 vol %.

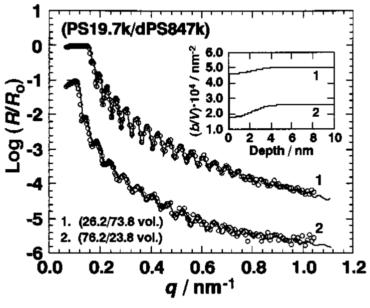

Figure 5. Neutron reflectivity profiles for (PS19.7K/dPS847K) blend films containing 26.2 and 76.2 vol % PS. The inset shows the enlarged scattering length density profiles in the vicinity of the surface.

Figure 5 shows the scattering vector, q [$=(4\pi/\lambda)\sin\theta$], dependence of neutron reflectivity for the (PS19.7K/dPS847K) films with the bulk PS fraction of 26.2 and 76.2 vol %. Their film thicknesses were 135 and 101 nm, respectively. The data for the film with 76.2 vol % PS is offset by 1 decade for the sake of clarity. The solid lines denote the best-fit calculated reflectivity to the experimental data based on model scattering length density, (b/V), profiles shown in the inset of Figure 5. Since the calculated curves are in good agreement with the experimental data, it can be claimed that the model (b/V) profile corresponds well to the composition profile in the film along normal to the surface. Hence, the surface composition of the (PS19.7K/dPS847K) films was deduced from the (b/V) value at the depth of 0.5 nm, which might be comparable to the tip indentation depth for LFM and the analytical depth of SSIMS. For PS and dPS, the (b/V) values of 1.41×10^{-4} and 6.46×10^{-4} nm^{-2} were used, respectively. The results by NR measurements are also shown in Figure 3.

In Figure 3, the surface compositions in the (PS19.7K/dPS847K) blend films obtained by the different three methods are plotted altogether against the bulk blend ratio. Also, the surface composition in a similar blend film by Hariharan et al. using NR was shown in it.[16] Those are in excellent agreement with one another.

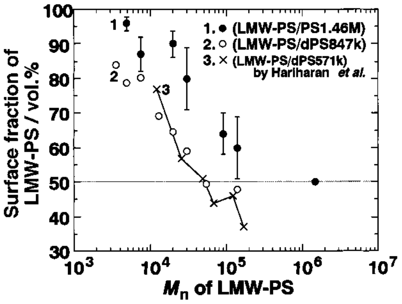

Figure 6. Surface compositions in (LMW-PS/PS1.46 M) and (LMW-PS/dPS847K) blend films as a function of M_n for LMW-PS. For a comparison, the data for (LMW-PS/dPS571K) blends by Hariharan et al. are plotted from ref 16.

Figure 3 makes it clear that the T_g^s measurement enables us to gain direct access to the surface composition in miscible binary blend films. Here, two points should be emphasized. The first point is that T_g^s based on our LFM measurement is extremely reliable. Otherwise, there is no reason why the surface compositions via the T_g^s measurements are in accordance with those by SSIMS and NR. The second is the following. In all of well-established surface characterization techniques, a component must be deuterated to confer a contrast between components. So far, it has been thought that it is experimentally impossible to examine the surface composition in mixtures of chemically identical two polymers, such as PS with bimodal molecular weight distribution. Jones and Richards have recently written in their book that "in order to be able to distinguish among chemically identical chains of different relative molecular masses, we need some form of labeling, but we have seen that polymer thermodynamics is so delicate that even deuterium labeling, which one might have thought of as being non-perturbative, itself can lead to substantial segregation phenomena."[17] On the other hand, our T_g^s method for the surface characterization proposed does not need any labeling procedures, meaning that it turns out to be possible to examine the surface composition in chemically identical binary blend films.

We now turn to the surface segregation in the (LMW-PS/PS1.46M) blend film as well as the (LMW-PS/dPS847K) system. Each higher M_n component in the blends was fixed to be PS with M_n of 1.46M and dPS with M_n of 847K, and the lower M_n (LMW) components for the blends were successively changed in terms of M_n. Figure 6 shows the surface composition in the (LMW-PS/PS1.46M) and the (LMW-PS/dPS847K) blends as a function of M_n for the LMW component. The (LMW-PS/PS1.46M) blend corresponds to PS with bimodal molecular weight distribution. The bulk blend ratio of the (LMW-PS/PS1.46M) and the (LMW-PS/dPS847K) was 50 and 51.6 vol % (=50 wt %), respectively. The surface composition in the (LMW-PS/PS1.46M) films was obtained by T_g^s measurements using eq 3.[18] Even in the case of the (PS140K/PS1.46M), the distinct partition of the PS140K to the surface was observed. The extent of the surface concentration of the LMW-PS became remarkable with decreasing M_n of the LMW-PS, as shown by filled circles in Figure 6. Although the surface segregation of the LMW component in chemically identical binary blend films has been theoretically predicted by Hariharan et al. on the basis of a compressible mean-field lattice model,[19] the experimental evidence has not been reported thus far. Hence, this is the first experimental report to prove quantitatively the surface segregation of the LMW component due purely to the entropic effect. In Figure 6, the surface composition of the (LMW-PS/dPS847K) film obtained by LFM and SSIMS measurements was also shown and compared with the reported results for the (LMW-PS/dPS571K) blends by Hariharan et al. using NR measurements.[20] They are in good agreement with each other. In the case of the mixture composed of LMW-PS and high molecular weight (HMW) dPS, which component is enriched at the surface is decided by the competition between energetic and entropic effects. For example, in the case of symmetric (PS/dPS) blends, the energetic effect based on the discrepancy of the polarizability between C−H and C−D bonds dominates, resulting in the surface enrichment of dPS. On the other hand, PS is partitioned to the surface if PS is much shorter than dPS. In general, a polymer chain present at the surface might have a flattened conformation.[21] This means that the number of possible conformations for a chain at the surface would decrease in comparison with the case where the chain has a random coil conformation in the interior bulk region. Hence, shorter chains suffer less of an entropic penalty than longer chains and thus are enriched at the surface to minimize the free energy of the system.

The extent of surface segregation is closely related to a dimensionless surface energy difference parameter, χ_s.[16] For the surface segregation based on molecular weight disparity, it can be given by

$$\chi_s = \chi_s^E + \frac{a\Delta\gamma}{k_B T} \tag{4}$$

where χ_s^E is the energetic contribution obtained from eq 5, a is the area occupied by a repeating unit of the chain, $\Delta\gamma$ is the surface free energy difference between components, and k_BT is the thermal energy.

$$\chi_s^E = -\frac{\epsilon_{hh} - \epsilon_{dd}}{2k_B T} \tag{5}$$

Here, ϵ_{hh} and ϵ_{dd} represent the interaction energy between two hydrogenated and two deuterated monomers in the bulk, respectively. The first term of eq 4 for the (PS/dPS) blend system was theoretically[22] and experimentally[16] revealed to be 0.005, whereas in the case of (PS/PS) blend, it should be 0. The aforementioned entropic contribution to the surface segregation, arisen from changing M_n, is included in the second term of eq 4. Thus, if the second term is addressed, the χ_s value can be deduced. Therefore, the M_n dependence of surface free energy, γ, for the PS was studied by contact angle measurements using Owens' method.[23] Pure water and diiodomethane were used as probe liquids for the measurements. Figure 7 shows such a plot. The solid and shaded curves denote the best-fitted ones under the assumptions that γ is proportional to $M_n^{-2/3}$ and M_n^{-1}, respectively.[24] Even though the surface energy difference between components in a blend film is quite small such as 0.08 mJ m^{-2},[5] the surface segregation of a component can be attained if chain length for the components is long enough. In contrast, the experimental error for the surface free energy based on the contact angle measurements is, at least, 0.3 mJ m^{-2}, as shown in Figure 7, although it is of importance to confirm experimentally that γ for the PS decreases with de-

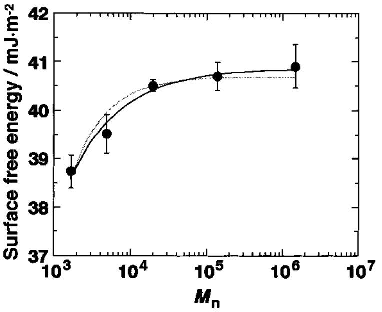

Figure 7. Molecular weight dependence of surface free energy for PS.

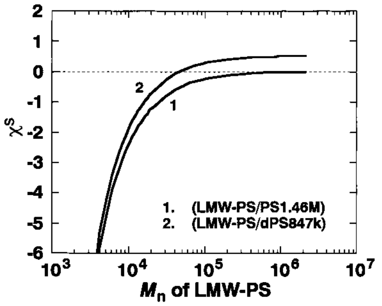

Figure 8. Dimensionless surface energy difference parameters for (LMW-PS/PS1.46 M) and (LMW-PS/dPS847K) blend films as a function of M_n for LMW-PS.

creasing its M_n. Hence, the next relation is used to estimate the second term of eq 4 instead of Figure 7.

$$\frac{a\Delta\gamma}{k_B T} = C_2\left(\frac{1}{r_1} - \frac{1}{r_2}\right) \qquad (6)$$

where r_i is the chain length for the component i and C_2 is a system specific constant. For the PS, C_2 assumes a value of -2.35.[16] Figure 8 shows the relation between χ_s and M_n of the LMW-PS for the (LMW-PS/PS1.46M) blend and the (LMW-PS/dPS847K) one. The 0 and negative values of χ_s mean that no segregation takes place at the surface and that the LMW-PS is enriched at the surface, respectively. Since in the case of the (LMW-PS/dPS847K) blend the χ_s value reaches 0 at M_n of approximately 40K, it is predicted that the surface composition of the LMW-PS becomes equal to the bulk one at this M_n. This is in good agreement with the experimental result, as shown in Figure 6. The χ_s difference between the two blends at a given M_n of the LMW-PS decreased with a decrease in M_n of the LMW-PS, and the same trend for the surface composition difference between the two blends was observed in Figure 6. Further, when the M_n of the LMW component becomes about 4K, it can be inferred from the χ_s value that the surface compositions of the LMW-PS in the both blend systems might be comparable. This conjecture is what is observed in Figure 6. Hence, it is clear that our results shown in Figure 6 are qualitatively reproduced by Hariharan's theory. Therefore, it seems reasonable to conclude that the surface characterization method proposed in this paper is powerful and can be used even for chemically identical binary polymer mixtures unlike the usual spectroscopic method.

Conclusions

An experimental method to characterize the surface concentration in miscible binary polymer mixtures, which is based on our T_g^s measurements using LFM, is proposed. The surface composition in PS/dPS blends so obtained by LFM was in good accordance with the results by SSIMS and NR measurements. Since our method does not need any labeling procedure, unlike usual spectroscopic techniques, the surface composition of the LMW component in the PS films with various binary molecular weight distributions was experimentally clarified. The dependence of the surface composition on M_n of the LMW-PS in such PSs was qualitatively in agreement with the theory by Hariharan et al.

Acknowledgment. This was in part supported by a Grant-in-Aid for Scientific Research (A) (#13355034) from the Ministry of Education, Science, Sports, and Culture, Japan, and by Tokuyama Science Foundation. Also, this work is partially supported in the utilization of the reactor by the Inter-Univ. Program for common use JAERI facility.

References and Notes

(1) Tanaka, K.; Takahara, A.; Kajiyama, T. *Macromolecules* **1997**, *30*, 6626.
(2) Affrossman, S.; Hartshorne, M.; Kiff, T.; Pethrick, R. A.; Richards, R. W. *Macromolecules* **1994**, *27*, 1588.
(3) Jones, R. A. L.; Norton, L. J.; Kramer, E. J.; Composto, R. J.; Stein, R. S.; Russell, T. P.; Mansour, A.; Karim, A.; Felcher, G. P.; Rafailovich, M. H.; Sokolov, J.; Zhao, X.; Schwarz, S. A. *Europhys. Lett.* **1990**, *12*, 41.
(4) Zhao, X.; Zhao, W.; Sokolov, J.; Rafailovich, M. H.; Schwarz, S. A.; Wilkens, B. J.; Jones, R. A. L.; Kramer, E. J. *Macromolecules* **1991**, *24*, 5991.
(5) Jones, R. A. L.; Kramer, E. J.; Sokolov, J.; Rafailovich, M. H.; Schwarz, S. A. *Phys. Rev. Lett.* **1989**, *62*, 280.
(6) Zink, F.; Kerle, T.; Klein, J. *Macromolecules* **1998**, *31*, 417.
(7) Hong, P. P.; Boerio, F. J.; Smith, S. D. *Macromolecules* **1993**, *26*, 1460.
(8) Kajiyama, T.; Tanaka, K.; Satomi, N.; Takahara, A. *Macromolecules* **1998**, *31*, 5150. Tanaka, K.; Takahara, A.; Kajiyama, T. *Macromolecules* **2000**, *33*, 7588.
(9) Satomi, N.; Takahara, A.; Kajiyama, T. *Macromolecules* **1999**, *32*, 4474. Satomi, N.; Tanaka, K.; Takahara, A.; Kajiyama, T.; Ishizone, T.; Nakahama, S. *Macromolecules* **2001**, *34*, 8761.
(10) Pu, Y.; Ge, S.; Rafailovich, M.; Sokolov, J.; Duan, Y.; Pearce, E.; Zaitsev, V.; Schwarz, S. *Langmuir* **2001**, *17*, 5865.
(11) Welp, K. A.; Co, C. C.; Wool, R. P. *J. Neutron Res.* **1999**, *8*, 37.
(12) Gordon, M.; Taylor, J. S. *J. Appl. Chem.* **1952**, *2*, 493.
(13) Bates, F. S.; Wignall, G. D. *Phys. Rev. Lett.* **1986**, *57*, 1429.
(14) Hammerschmidt, J. A.; Gladfelter, W. L.; Haugstad, G. *Macromolecules* **1999**, *32*, 3360.
(15) Vanden Eynde, X.; Bertrand, P.; Jérôme, R. *Macromolecules* **1997**, *30*, 6407.
(16) Hariharan, A.; Kumar, S. K.; Russell, T. P. *J. Chem. Phys.* **1993**, *98*, 4163.
(17) Jones, R. A. L.; Richards, R. W. *Polymers at Surfaces and Interfaces*; Cambridge University Press: Cambridge, 1999.
(18) Since both components in the blends are chemically the same, the K value in the Gordon−Taylor equation can be postulated to be 1.
(19) Hariharan, A.; Kumar, S. K.; Russell, T. P. *J. Chem. Phys.* **1993**, *99*, 4041.
(20) The M_n of the HMW components differs in the two. However, our data were directly compared with the data reported by Hariharan et al., because it was reported that the surface concentration of the LMW-PS in (LMW-PS/HMW-dPS) blends was insensitive to the M_n of the HMW-dPS. See ref 16.
(21) Bitsanis, I. A.; Brinke, G. *J. Chem. Phys.* **1993**, *99*, 3100.
(22) Hariharan, A.; Kumar, S. K.; Russell, T. P. *Macromolecules* **1991**, *24*, 4909.
(23) Owens, D. K.; Wendt, R. C. *J. Appl. Polym. Sci.* **1969**, *13*, 1740.
(24) Bender, G. W.; Gains, G. L., Jr. *Macromolecules* **1970**, *3*, 128.

MA011960O