3746 *Macromolecules* **1998,** *31,* 3746−3749

Surface Segregation of the Higher Surface Free Energy Component in Symmetric Polymer Blend Films

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Received August 18, 1997

Revised Manuscript Received March 9, 1998

Introduction. The surface aggregation state of polymer mixtures has been paid great attention for technological importance and scientific interest in the last decade, both experimentally[1] and theoretically.[2] It has been revealed that the surface structure is quite different from the bulk one due to the difference of energy state in the surface and the bulk regions. For instance, in the case of the symmetric binary polymer blend for which the degrees of polymerization for each component are almost equal, the surface is covered with the lower surface free energy component in the blend system in order to minimize the interfacial energy at the air−polymer interface.[1,2]

The surface segregation of the lower surface free energy component, however, does not necessarily occur in the case of the specific conditions described below. Authors investigated the surface aggregation state of the (higher molecular weight polystyrene (PS)/lower molecular weight poly(methyl methacrylate) (PMMA)) blend films and found that PMMA was preferentially segregated at the blend film surface, in the case that the molecular weight of PMMA was fairly small compared with that of PS.[3] The surface segreation of lower molecular weight PMMA with a higher surface free energy compared with PS can be explained mainly by two factors such as the smaller conformational entropic penalty and/or the larger translational entropy of PMMA chains at the film surface and the surface localization of chain end groups.

When the magnitude of the surface free energy of chain end groups is larger than that of main chain parts, the chain end groups migrate deeply into the bulk.[4] Koberstein et al. investigated the surface aggregation structure of an α,*ω*-dicarboxy-terminated poly(dimethylsiloxane) film and revealed that COOH chain end groups migrated deeply into the bulk.[5] Also, α,*ω*-dicarboxy-terminated polymer chains generally intermolecularly associative via hydrogen bonding between two COOH chain end groups, resulting in an increase in apparent molecular weight.

When both chain end groups of PS are modified to carboxyl groups, the apparent molecular weight of PS may increase due to hydrogen-bonding formation between COOH chain end groups. Then, the symmetric (PS/PMMA) blend system behaves apparently like the (higher molecular weight PS/PMMA) system. The purpose of this study is to realize the surface segregation of the higher surface free energy PMMA component in the symmetric (PS/PMMA) mixture by the end group modification.

Table 1. Characterizations of Polymers Used in This Study

sample	M_n[a]	M_w/ M_n[a]	γ_{sv}/mJ·m^{-2} [b]	f[c]	source
PS	4.9k	1.08	41.2		synthesized
α,*ω*-PS(COOH)$_2$	12k	1.09	41.2	1.98	Polymer Source, Inc.
PMMA	4.2k	1.10	43.7		synthesized
	13k	1.06	44.7		synthesized
α,*ω*-PMMA(COOH)$_2$	6.1k	1.10	45.5	1.85	Polymer Source, Inc.

[a] By gel permeation chromatography. [b] By static contact angle measurement using Owens' method. [c] Functionality.

Experimental Section. Materials and Film Preparation. Polymers used in this study were monodisperse PS, α,*ω*-dicarboxy-terminated PS (α,*ω*-PS-(COOH)$_2$), PMMA, and α,*ω*-dicarboxy-terminated PMMA (α,*ω*-PMMA(COOH)$_2$). Monodisperse PS and PMMA were synthesized by living anionic polymerization using *sec*-butyllithium as an initiator. Thus, the chemical structures of both end groups were the *sec*-butyl group and proton-terminated repeating unit, respectively. α,*ω*-PS(COOH)$_2$ and α,*ω*-PMMA(COOH)$_2$ were purchased from Polymer Source Inc. The initiator used for the preparation of α,*ω*-PS(COOH)$_2$ and α,*ω*-PMMA(COOH)$_2$ was lithium naphthalene. The carboxyl end groups were introduced by reacting the living end with highly purified CO_2 gas. The M_w and M_n were evaluated from gel permeation chromatography (GPC). The functionality was determined by acid−base titration in toluene/methanol with NaOH, using phenolphthalein as indicator. Table 1 shows the number-average molecular weight, M_n, the polydispersity index, M_w/M_n, where M_w denotes the weight-average molecular weight, and the surface free energy, γ, at 293 K. Three blends such as (α,*ω*-PS(COOH)$_2$ with M_n of 12k/PMMA with M_n of 13k), (PS with M_n of 4.9k/PMMA with M_n of 4.2k), and (PS with M_n of 4.9k/α,*ω*-PMMA(COOH)$_2$ with M_n of 6.1k) were prepared. The following number denotes M_n. All blend ratios were fixed at (50 wt %/50 wt %). The blend films were coated from a 2 wt % toluene solution onto a cleaned silicon water with a native oxide layer by spin coating at 2 krpm. The blend films prepared were kept under vacuum at 293 K for more than 72 h to remove the residual solvent. The thickness of the blend films evaluated by ellipsometry was ca. 80 nm. It was reported that the (PS-1.4k/PMMA-12k) (50:50) blend system exhibited the upper critical solution temperature (UCST) type phase diagram with a UCST of 453 K.[6] On the basis of the atomic force microscopic observation, it was confirmed that the surface of the (α,*ω*-PS(COOH)$_2$-12k/PMMA-13k) blend film was in a phase-separated state, whereas the surface for the (PS-4.9k/PMMA-4.2k) and (PS-4.9k/α,*ω*-PMMA(COOH)$_2$-6.1k) films was in a phase-mixing state due to the smaller M_n. These surface phase states did not change after annealing at 393 K for 24 h.

Surface Characterization. The surface chemical compositions of the blend films were investigated on the basis of X-ray photoelectron spectroscopic (XPS) measurement. The XPS spectra were obtained with an ESCA 850 X-ray photoelectron spectrometer (Shimadzu Co. Ltd.). The XPS measurement was performed under conventional conditions with a Mg Kα X-ray source at

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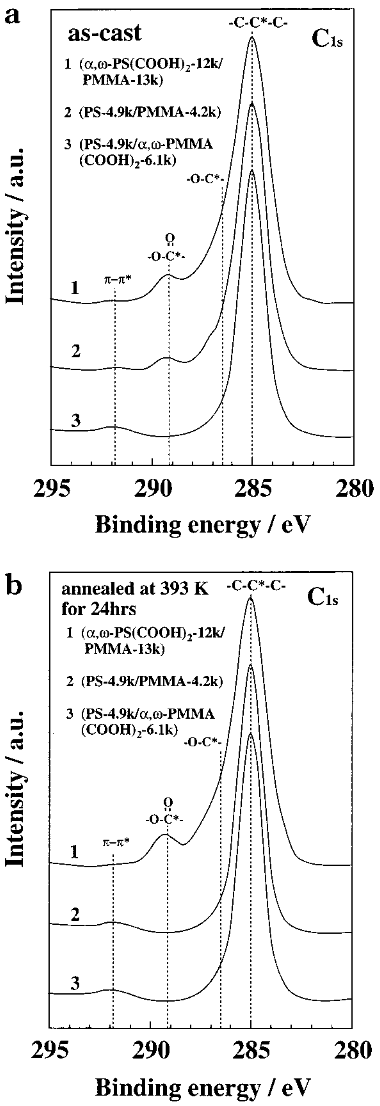

Figure 1. XPS C1s spectra of the (α,ω-PS(COOH)$_2$-12k/PMMA-13k), (PS-4.9k/PMMA-4.2k), and (PS-4.9k/α,ω-PMMA-(COOH)$_2$-6.1k) blend films: (a) as-cast blend films; (b) annealed ones at 393 K for 24 h.

8 kV and 30 mA. All C$_{1s}$ peaks corresponding to the neutral carbon were calibrated at a binding energy of 285.0 eV to correct for the charging energy shift. Since the magnitude of the emission angle of the photoelectron was 90 deg, the magnitude of the analytical depth from the outermost surface was ca. 10.5 nm.[7]

Results and Discussion. Figure 1a shows the XPS C$_{1s}$ spectra of the as-cast (α,ω-PS(COOH)$_2$-12k/PMMA-13k), (PS-4.9k/PMMA-4.2k), and (PS-4.9k/α,ω-PMMA-(COOH)$_2$-6.1k) blend films. Ordinary PS and PMMA have end groups composed of a *sec*-butyl group and a proton-terminated repeating unit. In the cases of the as-cast (α,ω-PS(COOH)$_2$-12k/PMMA-13k) and (PS-4.9k/PMMA-4.2k) blend films, the C$_{1s}$ peaks corresponding to the neutral, ether, and carbonyl carbons were clearly observed at 285.0, 286.5–287.0, and 289.0 eV, respectively. Also, the shake-up peak corresponding to the $\pi-\pi^*$ transition of the aromatic carbon was observed at 291.5–292.0 eV. On the other hand in the case of the (PS-4.9k/α,ω-PMMA(COOH)$_2$-6.1k) blend film, the peaks corresponding to the ether and carbonyl carbons were not observed and the peak shape agreed well with that of the PS homopolymer film. Therefore, it is apparent that in the cases of the as-cast (α,ω-PS-(COOH)$_2$-12k/PMMA-13k) and (PS-4.9k/PMMA-4.2k) films, both PS and PMMA are present in the surface, whereas, in the case of the as-cast (PS-4.9k/α,ω-PMMA-(COOH)$_2$-6.1k) blend film, the air–polymer interface is almost completely covered with PS. Since the solvent was evaporated fairly fast from the film, it might be considered that molecular chains in the as-case film were frozen in a nonequilbrium state. In order to investigate the surface molecular aggregation state in a quasi-equilibrium state, an annealing treatment of the blend films was carried out at 393 K for 24 h. Figure 1b shows the XPS C$_{1s}$ spectra of the (α,ω-PS(COOH)$_2$-12k/PMMA-13k), (PS-4.9k/PMMA-4.2k), and (PS-4.9k/α,ω-PMMA(COOH)$_2$-6.1k) blend films after annealing at 393 K for 24 h. Since the spectra shape for the (α,ω-PS(COOH)$_2$-12k/PMMA-13k) and (PS-4.9k/α,ω-PMMA-(COOH)$_2$-6.1k) blend films did not change before and after annealing, it appears that the surface structure being in a quasi-equilibrium state is formed even before annealing. On the other hand, the spectrum for the (PS-4.9k/PMMA-4.2k) blend film was drastically changed after annealing. Thus, these results clearly indicate that the formation rate of the surface structure for the blend film of which polymer chains have COOH chain ends is extremely fast compared with that of the blend film composed of proton-terminated polymer chains.

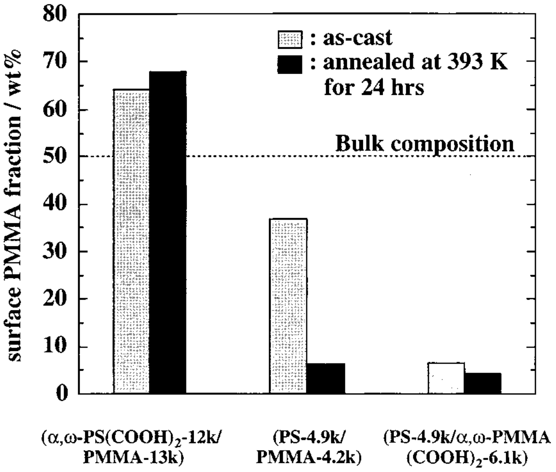

Figure 2. Surface chemical composition of the (α,ω-PS-(COOH)$_2$-12k/PMMA-13k), (PS-4.9k/PMMA-4.2k), and (PS-4.9k/α,ω-PMMA(COOH)$_2$-6.1k) blend films before and after annealing.

The surface chemical composition was evaluted on the basis of XPS studies in order to analyze quantitatively the surface aggregation state of the blend films. Figure 2 shows the surface PMMA weight fraction for three blend films, (α,ω-PS(COOH)$_2$-12k/PMMA-13k), (PS-4.9k/PMMA-4.2k), and (PS-4.9k/α,ω-PMMA(COOH)$_2$-6.1k), before and after annealing at 393 K for 24 h. Since the XPS spectrum of the α,ω-PS(COOH)$_2$ film did not show the peak assigned to the carbonyl carbon and corresponded well to that of the PS film, it was assumed that the carbonyl carbon peak observed in the C$_{1s}$ spectrum of the (α,ω-PS(COOH)$_2$-12k/PMMA-13k) blend film resulted from only the PMMA component. In the case of the (α,ω-PS(COOH)$_2$-12k/PMMA-13k) blend film, the surface PMMA fraction was ca. 65% and was higher than the PMMA weight fraction of 50% in the bulk. Thus, it seems reasonable to conclude that PMMA is preferentially segregated at the air–polymer interface even though PMMA has the main chain with a higher surface free energy compared with PS. The surface

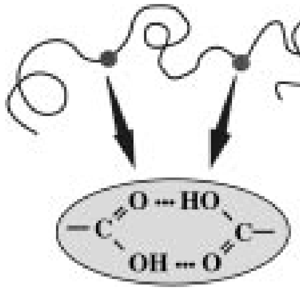

Figure 3. Schematic representation of the molecular aggregation state of the α,ω-PS(COOH)$_2$ film at 293 K.

molecular aggregation state of the (α,ω-PS(COOH)$_2$-12k/PMMA-13k) blend film was quite different from those for another blend film, as shown in Figure 2. In the case of the (PS-4.9k/α,ω-PMMA(COOH)$_2$-6.1k) blend film, the surface PMMA fraction was ca. 5% and was extremely low in comparison with the bulk composition of 50%. Also, in the case of the (PS-4.9k/PMMA-4.2k) blend film, the surface composition remarkably depended on annealing, as mentioned above, and the magnitudes of surface PMMA fraction were 37% and 6.2% before and after annealing, respectively. The results mentioned above indicate that the surface of the (PS-4.9k/PMMA-4.2k) and the (PS-4.9k/α,ω-PMMA-(COOH)$_2$-6.1k) blend films is almost completely covered with PS in order to minimize the interfacial free energy at the surface.

In the case of polymer chains with carboxyl end groups, it is reasonable to consider that the polymer chains may intermolecularly associate with another chain via hydrogen bonding between two carboxyl groups. Figure 3 shows the model describing a molecular association state of the α,ω-dicarboxy-terminated polymer chains. In order to confirm the intermolecular association of the polymer chains, two experiments were carried out as follows. First, the bulk glass transition temperature, T_g, of the α,ω-PS(COOH)$_2$-12k film was evaluated by using differential scanning calorimetry (DSC). In general, it is well-known that the bulk T_g is proportional to a reciprocal of the molecular weight because bulk T_g is a function of the concentration of chain end groups.[8] Thus, if the magnitude of bulk T_g for α,ω-PS(COOH)$_2$-12k is higher than that of proton-terminated PS-12k, it can be concluded that the α,ω-PS(COOH)$_2$ chains show an apparent increase in molecular weight, that is, an apparent decrease in chain end group concentration due to the intermolecular association of chain ends. Bulk T_g of α,ω-PS(COOH)$_2$-12k evaluated by DSC was 385 K, which corresponded to the proton-terminated PS with M_n more than 100k.[9] Thus, it seems reasonable to conclude that the α,ω-PS-(COOH)$_2$ chains are intermolecularly associated in the solid state. Second, Fourier transform infrared spectroscoic (FTIR) measurement, which is a direct method to confirm the intermolecular association, of the α,ω-PS(COOH)$_2$-12k film was carried out at 293 K. Figure 4 presents the FTIR spectrum of the α,ω-PS(COOH)$_2$-12k film at 293 K. The spectrum shows two absorption peaks at around 1710 and 1750 cm^{-1} corresponding to the stretching vibration of hydrogen-bonded and free carbonyl groups, respectively.[10] Thus, the FTIR result again clearly indicates that the end groups of α,ω-PS-(COOH)$_2$s are associated in the solid film.

In the case of the (higher molecular weight PS/lower molecular weight PMMA) blend films, PMMA is preferentially segregated at the film surface, even though the magnitude of the surface free energy for PMMA is higher than that of PS.[3] This surface segregation of PMMA can be explained in terms of entropic and enthalpic reasons. Since an amorphous polymer chain in the bulk region has a random coil conformation, its conformational entropy increases with an increase in the molecular weight. The conformational entropy of a polymeric chain at the surface is fairly smaller than that of a chain existing in the bulk because a polymer chain at the surface is compressed along the direction perpendicular to the film surface.[11] The difference in the conformational entropy of a polymer chain at the surface and in the bulk, corresponding to the penalty of the free energy at the film surface, increases with an increase in the molecular weight. Thus, from the standpoint of the conformational entropy, the surface segregation of the smaller molecular weight component is preferable. Also, the surface segregation of the lower molecular weight component can be understood by taking account of the larger translational entropy of a chain existing at the air–polymer interface as well as the conformational entropic penalty. In the case of the (α,ω-PS-(COOH)$_2$-12k/PMMA-13k) blend, as mentioned above, an apparent molecular weight of an α,ω-PS(COOH)$_2$ chain is remarkably increased in comparison with that of the proton-terminated PMMA chain due to an intermolecular association via hydrogen bonding. Therefore, it seems apparent that PMMA is enriched at the surface of the (α,ω-PS(COOH)$_2$-12k/PMMA-13k) blend film even though PMMA has the main chain with a higher surface free energy.

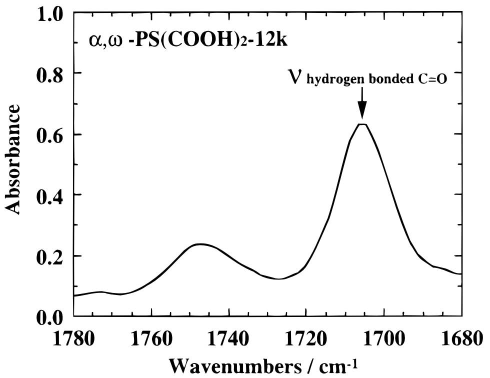

Figure 4. FTIR spectrum of the α,ω-PS(COOH)$_2$ film at 293 K.

Next, an effect of chain end groups on the surface segregation is discussed. When the magnitude of $(\gamma_e - \gamma_m)a^2$, where γ_e, γ_m, and a^2 are the surface free energy of chain end group and the main chain part and the cross-section area of segment, respectively, is larger than the magnitude of the thermal energy, kT, chain end groups are migrated deeply into the bulk region.[4] In the case of the carboxyl chain ends, both chain end groups are migrated deeply into the bulk,[5] resulting in the migration of the polymer chains jointed with both carboxyl end groups into the bulk. Thus, also from the standpoint of an effect of chain end groups, it is also reasonable to consider that PMMA chains are preferentially segregated at the surface in the case of the (α,ω-PS(COOH)$_2$-12k/PMMA-13k) blend film.

In conclusion, the surface molecular aggregation states of three blend films, (α,ω-PS(COOH)$_2$-12k/PMMA-13k), (PS-4.9k/PMMA-4.2k), and (PS-4.9k/α,ω-PMMA-(COOH)$_2$-6.1k), were investigated. The surface of the

(PS-4.9k/PMMA-4.2k) and (PS-4.9k/α,ω-PMMA$(COOH)_2$-6.1k) blend films was covered with PS. On the other hand, PMMA was enriched at the film surface in the case of the (α,ω-PS$(COOH)_2$-12k/PMMA-13k) blend. The surface segregation of PMMA, which has the main chain with a higher surface free energy, can be attributed to an apparent increase in M_n due to an intermolecular association of PS chains via hydrogen bonding and/or the preferential migration of carboxyl end groups into the bulk region.

Acknowledgment. This work was partially supported by a Grant-in-Aid for COE Research and Scientific Research on Priority Areas, "New Polymers and Their Nano-Organized Systems" (No. 277/08246239), from The Ministry of Education, Science, Sports, and Culture, and by Research Fellowships of the Japan Society for the Promotion of Science for Young Scientists.

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MA971247S