# Elimination of Surface Enrichment in Polymer Blends via Interpolymer Complexation

**Shiyong Liu,[†] Ming Jiang,*[,†] Chi-Ming Chan,*[,‡] and Lu-Tao Weng[§]**

*Institute of Macromolecular Science and Laboratory of Molecular Engineering of Polymers, Fudan University, Shanghai 200433, China; Department of Chemical Engineering, Biotechnology Research Institute, Hong Kong University of Science and Technology, Clear Water Bay, Hong Kong; and Materials Characterization and Preparation Facility, Hong Kong University of Science and Technology, Clear Water Bay, Hong Kong*

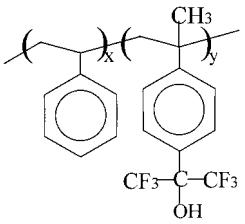
*Received August 17, 2000*
*Revised Manuscript Received January 4, 2001*

## Introduction

Since the early 1980s, studies on surface composition and structure in multicomponent polymer systems have been extensively conducted because of the significant effect of the surface composition on a variety of technically important properties of polymer blends with respect to applications in numerous fields.[1,2] One of the most outstanding conclusions in this field of research is that the polymer constituent having the lower surface energy will migrate to the surface leading to its surface enrichment. As a result of minimizing the air−polymer interfacial free energy, this phenomenon has been found for either immiscible[3] or miscible[4] polymer blends. For example, by using X-ray photoelectron spectroscopy (XPS) and low-energy ion scattering spectroscopy (ISS) in the immiscible blends polycarbonate (PC) and poly(dimethylsiloxane) (PDMS) with concentration of PDMS less than 11% in bulk, the surface concentration of PDMS was found to reach as high as 85% over the topmost 5 nm.[3a] Generally, miscibility does not alter this preferential placement of one component at the surface. The well-known miscible blend of PS and poly(vinyl methyl ether) (PVME) was found to exhibit a pronounced surface enrichment of PVME as the surface tension of PVME is lower compared to that of PS. In addition, block copolymers, in which the constituent chains are connected by chemical bonds, were reported to possess such surface-excess behavior as well.[3,5] However, some studies[3a] found that the block copolymer showed less surface preference than the corresponding homopolymer blends, and some[3b,5] found the opposite. In short, regarding the surface enrichment, no matter whether a polymer pair is miscible or immiscible and no matter whether it is a simple blend or block copolymer, the pair does show surface segregation provided a certain difference in surface free energy exists between the two constituents. In this note we report our recent study on surface composition of a series of polymer blends with controllable hydrogen bonding between the constituents showing completely different behavior from those reported in polymer blends so far.

It is well-known that, by introducing hydrogen bonding into an otherwise immiscible polymer blend via modifying one of the polymer component with some interaction groups, the blend is likely to become miscible.[6−8] In our long-term study on this subject we found that, by gradually increasing the density of the specific interaction groups, the miscible blend could further form interpolymer complexes.[8] Complexation in blend solutions can be judged by the appearance of a negative deviation in the curves of the reduced viscosity vs blend composition from the additivity law and the formation of interpolymer aggregates observed by light scattering, etc. Usually, complexation in solutions is accompanied by precipitation. It is believed that two different types of polymer chains are randomly mixed in a miscible blend while the segments of the component polymers are paired in complexes.[8,9] This striking difference in chain arrangement between miscible blends and complex blends is expected to cause quite different surface properties.

**Scheme 1. Chemical Structure of PS(OH)**




A series of polymer pairs consisting of poly(4-vinylpyridine) (PVPy) serving as proton acceptor and modified polystyrene, i.e., poly(styrene-*co*-*p*-(hexafluoro-2-hydroxyisopropyl)-α-methlystyrene) (PSOH) (Scheme 1), as proton donor were chosen for this study according to the following reasons. (1) The content of hydroxyl groups in PS(OH) and the consequent hydrogen-bond density in the blends can be easily controlled by changing feed composition in copolymerization of the two monomers. (2) Only PVPy contains nitrogen which makes it easy to measure the surface composition of the blends by XPS. (3) As we can see below, the surface energy of PS(OH) shows actually no change with its hydroxyl content. On the basis of this valuable character, we are able to attribute the changes observed in the surface behavior of the PS(OH)/PVPy blends with the hydroxyl content in PS(OH) to the complexation.

## Experimental Section

The hydroxyl-containing monomer *p*-(hexafluoro-2-hydroxyisopropyl)-α-methylstyrene (HFMS) was synthesized from *p*-chloromethylstyrene via the Gringnard reaction with hexafluoroacetone. Copolymers of styrene and HFMS were prepared by copolymerization in benzene at 60 °C using 2,2′-azobis(isobutyronitrile) (AIBN) as initiator and purified.[10] By varying the feed composition, a series of PS(OH) with different HFMS contents in the range 1.0−49 mol % were obtained. The HFMS content in the copolymers was determined by fluorine analysis.

PVPy was produced through radical polymerization of 4-vinylpyridine and purified. The related characterization data of PVPy and PS(OH) are listed in Table 1.

The samples for XPS measurements were prepared as follows. A blend solution of PS(OH) copolymer and PVPy was obtained by mixing the same amount of each polymer solution in chloroform ($CHCl_3$) at a concentration of 10 g/L under stirring. Depending on the HFMS contents in PS(OH), the mixed solutions might remain clear or form interpolymer complex precipitate. For PS(OH)-1/PVPy, PS(OH)-3/PVPy, and PS(OH)-5/PVPy, the clear solutions were spin-cast at 3800 rpm

[†] Fudan University.
[‡] Biotechnology Research Institute, Hong Kong University of Science and Technology.
[§] Materials Characterization and Preparation Facility, Hong Kong University of Science and Technology.

10.1021/ma001453r CCC: $20.00 
Published on Web 04/18/2001

**Table 1. Characteristic Data of PS(OH) and PVPy Samples**

| sample code | HFMS content/(mol %) | $M_n/10^4$ (g/mol) | $M_w/M_n$ | $T_g$ (°C) |
|---|---|---|---|---|
| PS | | 1.9 | 1.05 | 98.5 |
| PS(OH)-1 | 1 | 3.68 | 1.51 | 97.2 |
| PS(OH)-3 | 3.2 | 4.65 | 1.31 | 99.1 |
| PS(OH)-5 | 5.1 | 3.22 | 1.48 | 100.0 |
| PS(OH)-8 | 8.3 | 3.87 | 1.52 | 101.3 |
| PS(OH)-12 | 12.4 | 3.41 | 1.27 | 105.3 |
| PS(OH)-21 | 20.6 | 2.54 | 1.83 | 112.5 |
| PS(OH)-34 | 33.8 | 1.33 | 1.52 | 129.4 |
| PS(OH)-49 | 49.2 | 1.05 | 1.61 | 122.2 |
| PVPy | | 3.52[a] | | 146 |

[a] Determined from intrinsic viscosity in ethanol using $[\eta] = 2.5 \times 10^{-2} M_\eta^{0.68}$.

onto silicon wafers to obtain films with thickness of about 200−230 nm. At room temperature when the HFMS contents reached or exceeded 8 mol %, the solutions became turbid as interpolymer complex formed. The precipitate was then separated by centrifugation, washed with $CHCl_3$ three times, and kept in $CHCl_3$. The slightly swelled precipitates were pressed onto a silicon wafer for producing thin and smooth films. The films were then dried under vacuum at room temperature overnight. The bulk compositions of the complexes were determined from fluorine elemental analysis. DSC measurements were conducted with a differential scanning calorimeter (DSC-50, Shimadzu) at a heating rate of 10 °C/min.

The surface chemical composition and the binding energy were obtained from XPS spectra with a PHI 5600 multitechnique system equipped with a monochromatic Al Kα X-ray source. A pass energy of 23.4 eV was used. All core-level spectra were referenced to the C 1s neutral carbon peak at 285.0 eV. The emission angle (the angle between the surface normal and the axis of the analyzer) of the photoelectron was 45°, corresponding to a sampling depth of approximately 47 Å.

## Results and Discussion

As mentioned in the Experimental Section, PS(OH)-1/PVPy, PS(OH)-3/PVPy, and PS(OH)-5/PVPy blend solutions were clear. However, the corresponding blends showed different phase behavior; i.e., PS(OH)-1/PVPy and PS(OH)-3/PVPy blends were immiscible, showing two distinct $T_g$'s. PS(OH)-5/PVPy was miscible which shows only one $T_g$. Mixing the chloroform solutions of PS(OH)-8 and PVPy led to light precipitation, indicating that complexation at least partially occurred. As the hydroxyl content increased further to 12 mol % or more, severe precipitation took place. Such complexes, as expected, showed one $T_g$, which was higher than the calculated value by the additivity law.

The XPS results on all PS(OH)/PVPy blend films showed the presence of only four elements: carbon, oxygen, fluorine, and nitrogen. No signal from the silicon substrate and other contaminants were detected. Figure 1 shows the C 1s spectra of PS(OH)-3/PVPy, PS(OH)-21/PVPy, and PS(OH)-49/PVPy blends. The C 1s spectra can be resolved into five component peaks, namely, a hydrocarbon peak at 285.0 eV, the $C-(CF_3)_2OH$ peak at 288.6 eV, the $\pi-\pi^*$ shake-up satellite peak at 291.6 eV, the $CF_3$ peak at 293.4 eV, and the $C-N$ peak at 286.0 eV.[11,12]

The N 1s spectrum of PVPy shows a single nitrogen environment with a bond energy (BE) of 399.0 eV.[13] The N 1s spectrum of immiscible PS(OH)-3/PVPy is nearly the same as pure PVPy. When the HFMS in PS(OH) content reaches 5 mol %, the peak shifts slightly to the higher-BE ends, indicating that the nitrogen in the blends becomes slightly more electropositive. The N 1s peak of the PS(OH)/PVPy blends with HFMS content

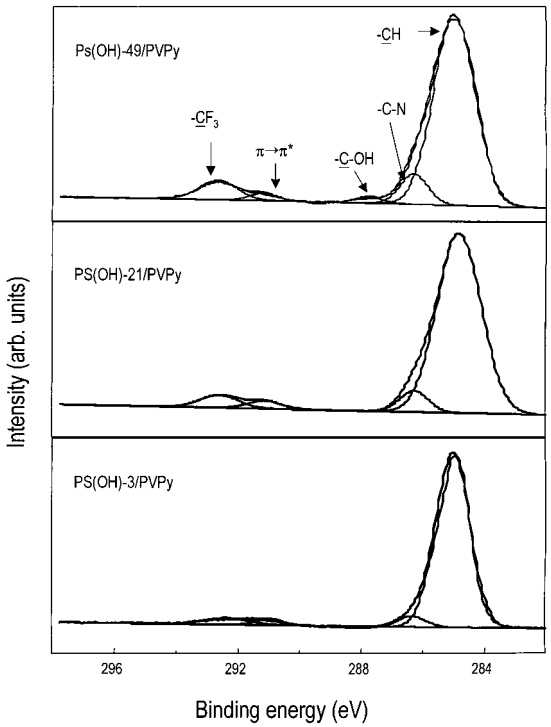



**Figure 1.** High-resolution C 1s XPS spectra of PS(OH)-3/PVPy, PS(OH)-21/PVPy, and PS(OH)-49/PVPy blends.

**Table 2. Characteristic Data of PS(OH)/PVPy Blends**

| sample code | $T_g$ (°C) | bulk comp (PS(OH), mol %) | surf. comp (PS(OH), mol %) |
|---|---|---|---|
| PS/PVPy | 99.0/145.5 | 50.2 | 99.55 |
| PS(OH)-1/PVPy | 104.1/143.2 | 49.8 | 89.26 |
| PS(OH)-3/PVPy | 106.5/132.4 | 48.89 | 80.82 |
| PS(OH)-5/PVPy | 117.8 | 48.13 | 70.74 |
| PS(OH)-8/PVPy | 132.2 | 55.15 | 70.40 |
| PS(OH)-12/PVPy | 149.3 | 52.84 | 60.81 |
| PS(OH)-21/PVPy | 160.4 | 49.87 | 50.90 |
| PS(OH)-34/PVPy | 166.1 | 46.81 | 44.33 |
| PS(OH)-49/PVPy | 176.5 | 42.62 | 40.47 |

higher than 5 mol % can be deconvoluted into two component peaks, i.e., the original one remaining at 399.0 eV and the new one at 400.0 eV. This indicates that there is almost no proton transfer between hydroxyl and pyridyl, as the peak associated with positively charged pyridinium ions is around 401.5 eV.[13] When HFMS content of PS(OH) increases further, the fraction of high-BE peak in the N 1s spectrum goes up considerably, indicating that more pyridyl groups in PVPy are hydrogen bonded to hydroxyl of PS(OH).

Table 2 compared the bulk and surface compositions of the blends of PVPy and PS(OH) with different hydroxyl contents but similar bulk composition. The surface and bulk compositions were calculated from fluorine analysis and the XPS N/C peak area ratio, respectively. First, remarkable surface enrichment was found for the immiscible blends; namely, in PS/PVPy, the surface is completely covered by PS(OH), and in PS(OH)-1/PVPy and PS(OH)-3/PVPy, the concentration of PS(OH) on the surface is as high as 80−90%. This is expected since PS has much lower surface free energy (40.2 mJ $m^{-2}$) compared with PVPy (68.2 mJ $m^{-2}$).[14] For miscible PS(OH)-5/PVPy blends, the surface is also significantly enriched with PS(OH). As the hydroxyl content in PS(OH) increases further, the degree of the surface segregation pronouncedly decreases. We are particularly interested in finding that for the last three

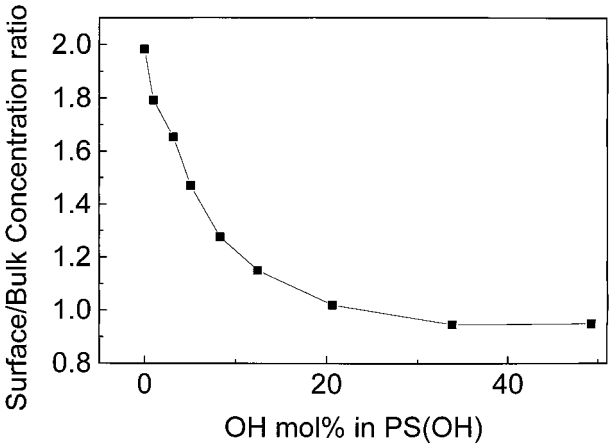



**Figure 2.** Ratio of PS(OH) concentrations of the surface to the bulk in PS(OH)/PVPy blends vs the HFMS content in PS(OH).

blends with respective hydroxyl content of 21, 34, and 49 mol %, forming interpolymer complexes; the chemical compositions of surface and bulk turn to be almost the same. Figure 2 shows the relationship between the degree of surface segregation and hydroxyl content in PS(OH) more clearly. The data clearly reveal that if the density of hydrogen-bonding interaction of a polymer blend reached a certain level leading to the unlike chains being combined together, the surface enrichment of the lower surface energy component can be greatly reduced or even completely eliminated. As far as we know, this is the first series of free surface-segregation blends found experimentally which are composed of component polymers with substantial surface energy difference In addition, the results reflect the inherent dissimilarities in the physical states between complexes and conventional miscible blends.

As mentioned above, there is a significant difference in surface energy between PS and PVPy which drives the surface segregation of PS in the blends. It is important to know how the surface energy of PS(OH) varies with the copolymer composition. As we reported previously,[12] by measuring the surface composition of the PS(OH) with hydroxyl content ranging from 3 to 50 mol % by XPS, it was found that the surface composition is the same as that of the bulk. It means that there is no fluorine segregation in PS(OH) over the wide range of the copolymer composition. More importantly, only little variation of the water contact angle of PS(OH) with hydroxyl content was found. It means that actually the possible decrease of the surface energy caused by the fluorinated groups was offset by the polar hydroxyl groups. This makes our discussion on the surface behavior of PS(OH)/PVPy much simpler; i.e., ,the difference in the surface energy between PVPy and PS(OH) is actually independent of the hydroxyl content in PS(OH). It implies that the dramatic decrease of the surface excess of PS(OH) to about zero when the hydroxyl content in PS(OH) reaches about 21 mol % can be exclusively attributed to the interpolymer complexation. It is understandable because in the complexes, migration of the low surface energy chains of PS(OH) to the surface is severely restricted by their counterparts, i.e., segment-paired chains of PVPy.

It is worth noting that all the samples for XPS measurements were prepared at room temperature without further annealing. Generally, annealing at a temperature below but close to $T_g$ for a long time would benefit approach to equilibrium. However, in the present case, as the $T_g$ for the complex blends is as high as 160−180 °C, annealing at such high temperature may cause disruption of the interpolymer hydrogen bonding as observed in our previous work.[15]

Finally, we would like to mention that Goh et al.[16] recently studied blends of poly(*N*-acryloyl-*N*′-phenylpiperazine) (PAPA) with respective proton-donating polymers, i.e., poly(styrenesulfonic acid) (PSSA), poly(vinylphosphonic acid) (PVPA), and poly(acrylic acid) (PAA). The three pairs were found to be able to form interpolymer complexes. The work concentrated on the nature of the specific interactions but without evaluating their data on surface compositions further. On the basis of the data of surface and bulk compositions reported in the paper, we found that there is a little surface segregation in the three groups of complexes. Particularly, for PAPA/PAA complexes , the surface composition was very close to the bulk composition as shown by the following data. For the blends of PAPA/PAA (22/78, 27/73, and 33/67) the bulk/surface compositions of PAPA are 0.22/0.23, 0.27/0.30, and 0.33/0.33, respectively. The data support our conclusion that interpolymer complexation can depress or even eliminate the surface segregation of the low surface energy component in polymer blends. However, this argument does not appear to be really conclusive as no data of the surface energy or surface tension for the constituent polymers are available in the paper.

**Acknowledgment.** This work was supported by National Natural Science Foundation of China (NNSFC, No. 59773023). This work was also supported by the Hong Kong Government Research Grand Council under Grant HKUST 9123/97P and the Biotechnology Research Institute under Grant TCMRPS/5/97.

## References and Notes

(1) Chan, C. M. *Polymer Surface Modification and Characterization;* Hauser: New York, 1994.
(2) Briggs, D. *Surface Analysis of Polymers by XPS and Static SIMS*; Cambridge University Press: Cambridge, 1998.
(3) For example: (a) Schmitt, R. L.; Gardella, J. A.; Salvati, L. *Macromolecules* **1986**, *19*, 648. (b) Thomas, H. R.; O'Malley, J. J. *Macormolecules* **1981**, *14*, 1316.
(4) For example: (a) Bhatia, Q. S.; Pan, D. H.; Koberstein, J. T. *Macromolecules* **1988**, *21*, 2166. (b) Jones, R. A. L.; Kramer, E. J.; Rafailovich, M. H.; Sokolov, J.; Schwarz, S. A. *Phys. Rev. Lett.* **1989**, *62*, 280.
(5) O'Malley, J. J.; Thomas, H. R.; Gee, G. M. *Macromolecules* **1979**, *12*, 966.
(6) Coleman, M. M.; Painter, P. C. *Prog. Polym. Sci.* **1995**, *20*, 1.
(7) Pearce, E. M.; Kwei, T. K. In *Polymer Solutions, Blends and Interface;* Noda, I., Rubingh, D., Eds.; Elsevier: Amsterdam, 1992.
(8) Jiang, M.; Li, M.; Xiang, M.; Zhou, H. *Adv. Polym. Sci.* **1999**, *142*, 121.
(9) Xiang, M.; Jiang, M.; Zhang, Y.; Wu, C.; Feng, L. *Macromolecules* **1997**, *30*, 2313. (b) Xiang, M.; Jiang, M.; Zhang, Y.; Wu, C. *Macromolecules* **1997**, *30*, 5339. (c) Jiang, M. *Macromol. Symp.* **1997**, *118*, 377.
(10) Cao, X.; Jiang, M.; Yu, T. *Makromol. Chem.* **1989**, *190*, 117.
(11) Li, L.; Chan, C. M.; Weng, L. T.; Xiang, M.; Jiang, M. *Macromolecules* **1998**, *31*, 7248.
(12) Liu, S.; Weng, L. T.; Chan, C. M.; Li, L.; Ho, K.-C.; Jiang, M. *Surf. Interface Anal.*, in press.
(13) Zhou, X.; Goh, S. H.; Lee, S. Y.; Tan, K. L. *Appl. Surf. Sci.* **1997**, *119*, 60.
(14) Jiang, X.; Tanaka, K.; Takahama, A.; Kajiyama, T. *Polymer* **1998**, *39*, 2615.
(15) Liu, S.; Pan, Q.; Xie, J.; Jiang, M. *Polymer* **2000**, *41*, 6919.
(16) Goh, S. H.; Liu, Y.; Lee, S. Y.; Huan, C. H. A. *Macromolecules* **1999**, *32*, 8595.

MA001453R