Surface Composition of Poly(methylphenylsiloxane)−Polystyrene Block Copolymers[†]

Stephen J. Clarson,*,1 James O. Stuart, and Craig E. Selby

Department of Materials Science and Engineering and the Polymer Research Center, University of Cincinnati, Cincinnati, Ohio 45221-0012

Ashok Sabata

Armco Research & Technology, Middletown, Ohio 45044-3999

Steven D. Smith and Arman Ashraf

Procter and Gamble Company, Miami Valley Laboratories, Cincinnati, Ohio 45239-8707

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ABSTRACT: The surface compositions of poly(methylphenylsiloxane) (PMPS) homopolymers and poly-(methylphenylsiloxane)−polystyrene (PMPS−PS) diblock copolymers have been analyzed using time-of-flight secondary ion mass spectrometry (TOFSIMS). The high surface sensitivity of this method, which probes samples to depths of a few Angstroms, showed the block copolymer samples to have both poly-(methylphenylsiloxane) and polystyrene segments present at the surface. These results may be contrasted with the behavior seen for poly(dimethylsiloxane) (PDMS) blocks and blends, where the low surface energy of the −[O−Si(CH₃)₂]− repeat units typically leads to surface segregation and complete PDMS surface coverage is seen. Investigation of the thermal characteristics of the block copolymers by differential scanning calorimetry revealed a single glass transition temperature, indicating a single phase morphology. The surfaces of the block copolymers also showed an enrichment of −Si(CH₃)₃ groups, which are the terminal groups of the PMPS, presumably due to the low surface energy of the trimethylsilyl groups.

Introduction

Over the last 20 years or so many investigations of poly(dimethylsiloxane)−polystyrene diblock and triblock copolymers have been reported.[2−11] More recently, the preparation and properties of poly(methylphenylsiloxane)−polystyrene[12−16] and poly(methyl(3,3,3-trifluoropropyl)siloxane)−polystyrene[17] diblock copolymers have also been described.

The low surface energy of poly(dimethylsiloxane) (PDMS) leads to many of its commercial applications.[18−20] Furthermore, the addition of small amounts of organic−PDMS block copolymers to the parent organic homopolymer typically leads to a saturation of the surface with siloxane.[9,21,22] McGrath and co-workers have made extensive use of angular-resolved X-ray photoelectron spectroscopy (XPS) to characterize the surface segregation of organic−PDMS blocks having a variety of architectures in the organic homopolymers.[9,22] An important result from these studies is that when the percent PDMS in the bulk is plotted against the log of percent siloxane at the surface for polycarbonate−PDMS alternating block copolymer in polycarbonate homopolymer, there is a critical concentration corresponding to ~1% PDMS in the bulk at which a marked increase in the surface concentration of PDMS is seen.[9,22]

Far less attention has been given to the surface properties of poly(methylphenylsiloxane) (PMPS), as it has a higher surface energy than PDMS due to the polarizable phenyl groups. PMPS has, however, shown very interesting surface characteristics for films on water, where a change from a spreading state to a nonspreading state was observed upon both increasing molar mass and increasing temperature.[23,24] The physics of such a "drying" transition for chain molecules was discussed previously by de Gennes.[25] In this publication we will describe an investigation of the surface compositions of poly(methylphenylsiloxane) (PMPS) homopolymers and poly(methylphenylsiloxane)−polystyrene (PMPS−PS) diblock copolymers analyzed using time-of-flight secondary ion mass spectrometry (TOFSIMS).

Experimental Section

Materials. The PS−PMPS block copolymers were prepared by anionic polymerization methods using standard vacuum/Schlenk line techniques and carefully purified reagents.[26] All glassware, transfer syringes, needles, etc. were flame dried and purged with nitrogen prior to use. The styrene was initiated using *sec*-butyllithium (1.3 M in cyclohexane) and the reaction vessel maintained at 60 °C throughout the polymerizations. All the reactions were carried out in cyclohexane which was stirred over sulfuric acid for 2 weeks to remove any olefin impurities, followed by washing, distillation, and further drying prior to use. To the cyclohexane-filled reactor, the desired quantity of purified styrene was added. The styryl anion was then titrated with *s*-BuLi to persistence of a yellow color. Immediately, the calculated amount of *s*-BuLi was charged, resulting in a color change from yellow to red. The polymerization was allowed to proceed to completion of the styrene reaction, and a small amount of the solution was sampled immediately prior to the crossover reaction. This sample was terminated using trimethylchlorosilane (CH₃)₃SiCl and analyzed by GPC.

The mixed *cis* and *trans* cyclic methylphenylsiloxane trimers [(CH₃)(C₆H₅)SiO]₃ were isolated from a reaction of methylphenyldichlorosilane (CH₃)(C₆H₅)SiCl₂ with zinc oxide[27] and were purified by distillation under vacuum and by pressure filtering of the desired solid from the viscous PMPS mixture. The purified mixed trimer was obtained in about 15% overall yield and was then enriched in the *cis* isomer and further purified by passing through an alumina column, before being added to the growing polystyrene chains. Crossover of the anion to the siloxane was successfully achieved by initially adding 10%
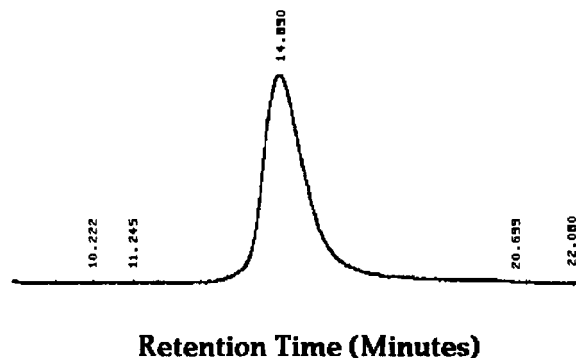
Retention Time (Minutes)

Figure 1. GPC of PS–PMPS diblock copolymer (CP-2).

Table 1. Number-Average Molar Masses M_n, Weight Percent PS, Glass Transition Temperatures T_g, and Structures of the Homopolymers (HP) and Diblock Copolymers (CP)

sample	structure	M_n/g mol^{-1}	wt % PS	T_g/K
HP-1	$(CH_3)_3SiO$–PMPS–$OSi(CH_3)_3$	12 900		240.0
HP-2	$(CH_3)_3SiO$–PMPS–$OSi(CH_3)_3$	47 300		240.1
HP-3	HO–PMPS–OH	93 000		240.5
CP-1	s-Bu–PS–PMPS–$OSi(CH_3)_3$	3 300	48.8	312.4
CP-2	s-Bu–PS–PMPS–$OSi(CH_3)_3$	12 700	68.2	315.8

of the PMPS trimer to be used and immediately adding tetrahydrofuran to the system (10%) as a promoter. The remaining siloxane trimer was added once the crossover was visibly completed. The polymerizations were terminated using trimethylchlorosilane. The resulting solutions were then neutralized using sodium bicarbonate, extracted, and dried and the solvents removed by rotary evaporation. The polymer samples were then reprecipitated from solution and extensively Soxhlet extracted with 2-propanol prior to being analyzed by GPC, ^{1}H, ^{13}C, and ^{29}Si NMR, and IR. The Waters GPC was calibrated using both PS standards and well-characterized PMPS homopolymer sharp fractions that we have described previously.[28] Their characteristics are listed in Table 1, and the polydispersities M_w/M_n of the precursor PS and the final blocks (see Figure 1) were less than 1.1, in each case. The copolymer compositions determined from the GPC results of the precursor chains and the GPC, ^{1}H NMR, and IR of the final blocks are given in Table 1.

The poly(methylphenylsiloxane) homopolymers were prepared by anionic ring-opening polymerization of cyclic tetramer $[(CH_3)(C_6H_5)SiO]_4$, as reported previously,[28] and had number-average molar masses M_n of 12 900, 47 300, and 93 000 g mol^{-1} and polydispersities of 1.15, 1.16, and 2.0, respectively. For the time-of-flight secondary ion mass spectrometry (TOFSIMS) the homopolymers and blocks were dissolved in chloroform and the samples coated onto glass or stainless steel substrates at room temperature. After exhaustive solvent removal, the samples were analyzed using TOFSIMS as described below.

Differential Scanning Calorimetry. Thermal analysis of the samples was carried out on a Mettler DSC 30 using a temperature profile as follows: a first heat from 25 to 150 °C at 20 °C min^{-1}; followed by a cool to −60 °C at 10 °C min^{-1}; and the final heat at 20 °C min^{-1} from −60 to 150 °C. The results for the blocks were taken from the second heating.

TOFSIMS Analysis. TOFSIMS analyses were performed on a Kratos PRISM instrument. It was equipped with a reflectron-type time-of-flight mass analyzer and a 25 kV liquid metal ion source of monoisotopic ^{69}Ga$^+$ ions with a minimum beam size of 500 Å. Positive and negative spectra were obtained at a pulse width of 10−50 ns, and a total integrated ion dose of about 10^{11} ions/cm^2. The mass resolution at 50 amu varied from $M/\Delta M = 1000$ at 50 ns pulse width to about 2500 at 10 ns pulse width. The area analyzed by the instrument is 1 mm^2. The spectra shown were recorded using a pulsed beam without scanning. Preliminary mapping on the samples showed a uniform distribution of the peaks over the complete area of the sample.
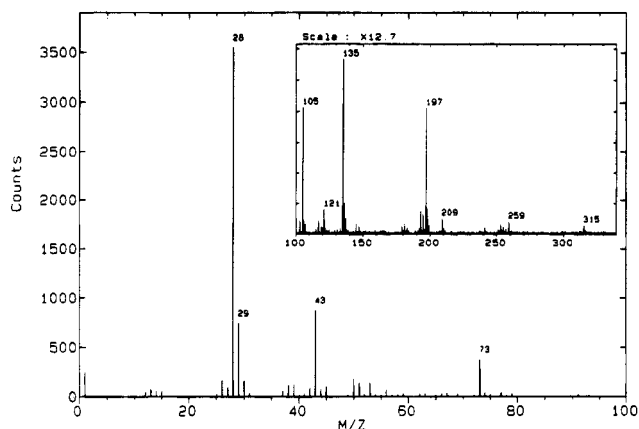

Figure 2. Positive TOFSIMS of $(CH_3)_3SiO$–PMPS–$OSi(CH_3)_3$ (HP-1).
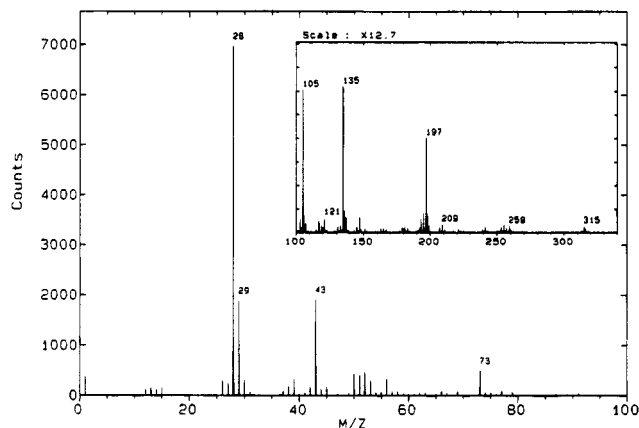

Figure 3. Positive TOFSIMS of $(CH_3)_3SiO$–PMPS–$OSi(CH_3)_3$ (HP-2).
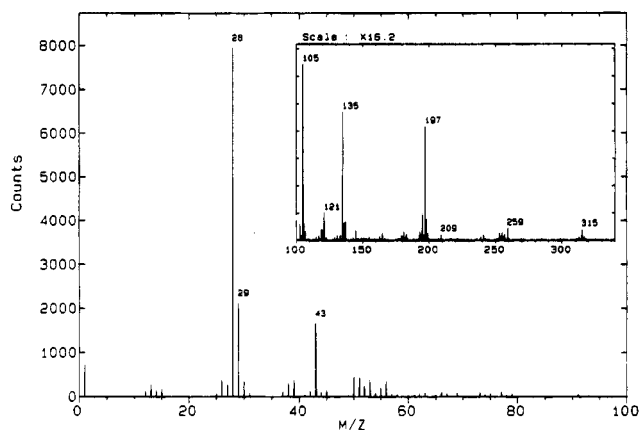

Figure 4. Positive TOFSIMS of HO–PMPS–OH (HP-3).

Results and Conclusions

The positive TOFSIMS spectra of the homopolymer and block copolymers are shown as Figures 2−6. The trimethylsilyl-terminated PMPS homopolymers $(CH_3)_3$-SiO–PMPS–$OSi(CH_3)_3$ show characteristic peaks at m/z 28, 29, 43, 73, 105, 121, 135, 197, 209, 259, and 315 (Figures 2 and 3). For the positive TOFSIMS spectrum of the PMPS homopolymer terminated with hydroxyl groups at both ends HO−PMPS−OH their was no significant peak at m/z 73 (Figure 4). The spectra of the PMPS homopolymers terminated with trimethylsilyl groups at both ends (see Figures 2 and 3), however, clearly show a peak at m/z 73. The peak at m/z of 73 therefore does not appear to result from a rearrangement of the polymer structure for PMPS. For the HO−
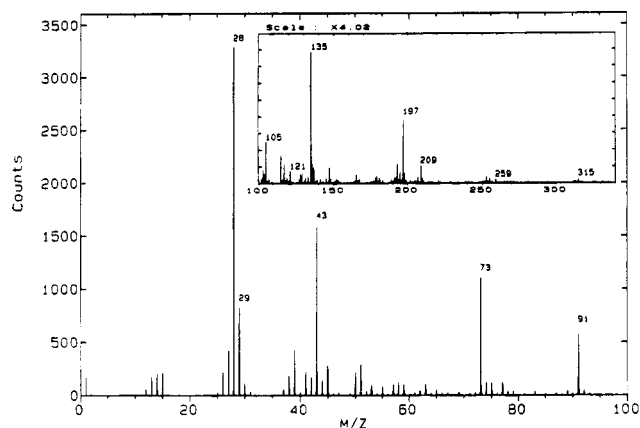
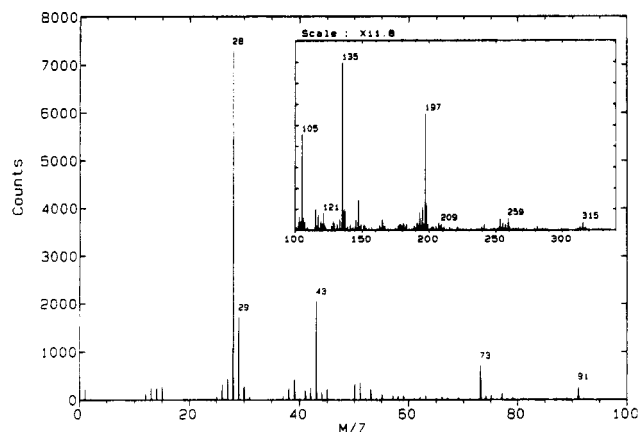**Figure 5.** Positive TOFSIMS s-Bu–PS–PMPS–OSi(CH₃)₃ (CP-1).

Figure 6. Positive TOFSIMS of s-Bu–PS–PMPS–OSi(CH$_3$)$_3$ (CP-2).

Figure 7. (A) DSC thermogram of s-Bu–PS–PMPS–OSi-(CH$_3$)$_3$ (CP-1). (B) DSC thermogram of s-Bu–PS–PMPS–OSi-(CH$_3$)$_3$ (CP-2).

PMPS–OH homopolymer the most dominant peak above m/z 100 is peak m/z 105 [Si(C$_6$H$_5$)]$^+$. By contrast the homopolymers and the block copolymers show peak m/z 135 [Si(C$_6$H$_5$)(CH$_3$)$_2$]$^+$ to be the dominant peak. Furthermore, as the amount of –OSi(CH$_3$)$_3$ terminal group decreases in relation to the siloxane chain length for the homopolymers and block copolymers, the ratio of peak m/z 135 to 105 decreases (see Figures 2, 3, 5, and 6). The absence of peak m/z 73 from the positive spectra of both the HO-PMPS-OH and of fully deuterated poly(dimethylsiloxane) –[O–Si(CD$_3$)$_2$]–[29] prepared in our laboratory would eliminate the possible contamination by small amounts of hydrogenous PDMS. The data thus indicate an effect of the chemical nature of the end group on the SIMS fragmentation/rearrangement of PMPS and is worth further investigation.

From the TOFSIMS spectra of the PS–PMPS blocks (see Figures 5 and 6) the Si$^+$ peak at m/z of 28 is obviously from the siloxane, as are the fragments at m/z of 43, 73, 105, 135, and 197, respectively. The peak at m/z of 91 is the tropylium cation C$_7$H$_7$$^+$, which is characteristic of the polystyrene. For the PS–PMPS (CP-1) block (Figure 5) there are more of the PS segments at the surface than for the PS–PMPS (CP-2) (Figure 6), despite the lower styrene content in the low molar mass copolymer. Investigation of the thermal characteristics of the block copolymers by differential scanning calorimetry revealed a single glass transition temperature (see Figures 7A and 7B), indicating a single phase morphology.[30,31] The PS–PMPS system is therefore not complicated by underlying block copolymer morphology effects for the molar masses and composi-
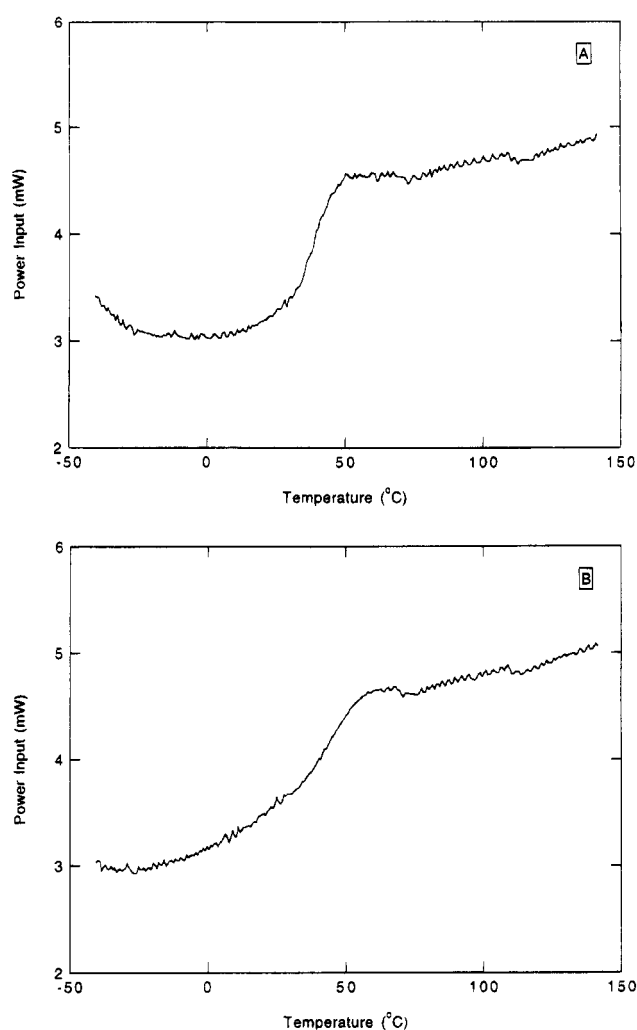
tions used in this study. In this context it is worth noting that some miscibility has been reported for low molar mass PS and PMPS homopolymer blends[32,33] and that a single glass transition T_g was reported for a PS–PMPS diblock copolymer ($M = 10\,500$, $\phi_{PS} = 0.49$).[16] Unlike PS–PDMS blocks of similar length,[11] the PS–PMPS (CP-2) does clearly show some PS at the surface (Figure 6). The driving force for a saturated surface layer of siloxane in the case of the PS–PDMS blocks[9,21,22] is the much lower surface energy of PDMS than of the PS.[34] This driving force for siloxane surface enrichment is much diminished in the case of PMPS, as the polarizable phenyl groups lead to a much higher surface energy in this system. We are only relating trends in peak intensities here, however, and not fully quantifying our findings on surface composition based upon peak intensities at this stage. It is however, worth noting that Thompson has shown TOFSIMS to be little affected by matrix effects[35] and that on the basis of peak intensities is, in a quantitative sense, more accurate than other surface analysis methods (e.g. XPS) for the analysis of blend compositions, etc.

There is some interest in the peak at m/z 73, which corresponds to Si(CH$_3$)$_3$$^+$ fragments. This is fairly pronounced for the spectra of the trimethylsilyl-terminated homopolymers and of the PS–PMPS blocks (see Figures 5 and 6) whose structure is s-Bu–PS–PMPS–OSi(CH$_3$)$_3$. One explanation of this observation is the

preferential orientation of the −Si(CH₃)₃ groups, which are the terminal groups of the PMPS in the block copolymer, to the surface. Chain ends are expected to be at surfaces for entropic reasons,[36,37] however, in the system studied here, the MPS −[(CH₃)(C₆H₅)SiO]− segments in both the blocks and the homopolymers have higher surface energies than the terminal trimethylsilyl groups −Si(CH₃)₃, and this latter effect would dominate. It is hoped that this hypothesis can be further tested from TOFSIMS of polysiloxanes terminated with −OSi(CD₃)₃ groups. It also appears that the silanol groups of the HO−PMPS−OH sample are not at the polymer surface—being polar and hydrogen bonded, such groups should be buried for thermodynamic reasons. This behavior has been indirectly inferred from many data[38] but not directly observed previously by a "molecular" method. Group contribution calculations by Koberstein and co-workers[39] on siloxanes having various terminal groups are consistent with the results of this investigation. The chemical nature of the end groups in the linear polysiloxanes can therefore clearly modify their surface behavior while they appear to have little or no effect on bulk physical properties, as has been shown in studies such as blend miscibility.[40]

Concluding Remarks

The surface composition of poly(methylphenylsiloxane)−polystyrene diblock copolymers have been analyzed using time-of-flight secondary ion mass spectrometry TOFSIMS. The high surface sensitivity of this method, which probes samples to depths of a few Angstroms (≪10 Å), showed the surface of the samples to have both poly(methylphenylsiloxane) and polystyrene segments. Thus PMPS does not exhibit the strong surface segregation behavior seen for other types of silicones and most notably for PDMS. The surfaces of the block copolymers appeared to show an enrichment of −Si(CH₃)₃ groups, which are the terminal groups of the PMPS, presumably due to the low surface energy of the terminal groups. While this end group enrichment effect is interesting and worthy of further investigations, this interpretation is supported by the absence of a peak at m/z 73 in the positive TOFSIMS spectra of both hydroxyl-terminated PMPS H[OSi(C₆H₅)(CH₃)]ᵧ− OH and of fully deuterated poly(dimethylsiloxane) which clearly do not contain the trimethylsilyl group. Differential scanning calorimetry revealed the PMPS−PS diblocks to have a single glass transition temperature and indicates a single phase system. The surface compositions of the PMPS−PS diblocks is not complicated by an underlying block copolymer morphology. Further studies of properties of a variety of polystyrene−[CH₃RSiO]ᵧ− block copolymers are in progress.

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References and Notes

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