# Ordering at Diblock Copolymer Surfaces

**Peter F. Green***

*Sandia National Laboratories, Albuquerque, New Mexico 87185-5800*

**Thomas M. Christensen**[†]

*Department of Physics, University of Colorado, Colorado Springs, Colorado 80933*

**Thomas P. Russell**

*IBM Almaden Research Center, San Jose, California 95120-6099*

*Received March 26, 1990*

ABSTRACT: The temperature dependence of the surface excess of a series of symmetric microphase-separated diblock copolymers of polystyrene (PS) and poly(methyl methacrylate) (PMMA) was determined by using X-ray photoelectron spectroscopy. For diblock copolymer systems in the strong segregation limit, under equilibrium conditions, a pure layer of PS was located at the surface, whereas for systems in the weak segregation limit, a layer composed of a mixture of PS and PMMA was located there. The surface excess of PS of a weakly segregated diblock copolymer system was observed to decrease with increasing temperature. We show that the chemical potential difference that favors PS at the surface decreases with increasing temperature. The segmental interactions in the vicinity of the surface are modified such that the surface should order at a temperature above the bulk microphase-separation transition (MST). The length scale over which the segmental interactions in the vicinity of the surface are perturbed is on the order of a statistical segment length. Finally, an estimate of the proximity of the weakly segregated system to the bulk MST is made based on the experimental data.

## Introduction

Below the bulk microphase-separation transition (MST), diblock copolymers order into spatially periodic structures that minimize the total free energy of the system. These structures, which exhibit varying symmetries that are dictated by the relative lengths of the components of the copolymer chain, are formed as a result of the connectivity of the components and the relative repulsive interactions between them.[1-3]

The interfacial properties of diblock copolymers are exploited for a variety of technological applications. Block copolymers behave like classical surfactants and for this reason are often blended with immiscible homopolymer/homopolymer mixtures in order to improve the mechanical properties of such systems. Block copolymers are also used as thin-film adhesives. In the area of microelectronics they are used as resists, and in the biomedical technology they are sometimes used where aspects of biocompatibility are important. In order to fully exploit the interfacial properties of diblock copolymer systems, a fundamantal understanding of their surface properties is important.

It is well-known in multicomponent systems, small molecule or polymeric, that the composition in the vicinity of an interface differs from the average bulk composition. In the special case of a free surface, the lowest surface energy component exhibits a preferential affinity for the surface.[4-8] Surface segregation effects are far more prevalent in polymeric than small-molecule systems because polymers are characterized by a very low combinatorial entropy of mixing and undergo microphase separation more readily (the combinatorial entropy of mixing in polymers is very small $\sim 1/N$, where $N$ is the number of segments that comprise the chain[9,10]). In a system that is microphase separated, the energy penalty for removing a chain from the bulk to the surface region is offset by a larger decrease in free energy, which results if this component is the lowest surface energy constituent. One should therefore expect surface segregation effects to be less severe in systems where there is a strong driving force for miscibility.

The behavior of copolymer surfaces differs from that of polymer blends for a number of reasons. In copolymers the constituents are connected; therefore, they cannot undergo large size scale phase separation as polymer blends do. Instead, they form spatially periodic phases on a molecular size scale. Unlike polymer blends the composition profile in the near surface region of diblock copolymers exhibits oscillations[11] that decrease exponentially in the bulk. This is a consequence of the connectivity of the segments. In polymer blends the oscillations are absent and the decay is exponential.[12]

In the past there have been a number of surface studies of block copolymers[5-8,11-21] using X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), and surface tension. Many of these measurements were performed on samples produced using solvents, where it has been shown that the nature of the solvent will affect the surface composition. XPS measurements (see refs 6 and 7, for example) show that in some situations the near surface region is composed of a pure layer of the lower surface energy component, and in other cases one finds that the surface is composed of both constituents. We[17] have shown in an earlier publication that the rate at which the solvent evaporates from the samples during preparation of the sample can also affect the near surface composition. Surface tension measurements[5] of a series of molten poly(ethylene oxide) (PEO)/poly(propylene oxide) (PPO) copolymers showed that the surface excess was chain-length dependent. As the chain length increased, the surface excess of PPO, the lower surface energy component, increased.

Using secondary ion mass spectroscopy (SIMS),[13] small-angle X-ray scattering (SAXS),[18] and neutron reflectivity,[15-17] we have shown that the bulk microstruc-

---

[†] Former address: Sandia National Laboratories, Albuquerque, NM 87185-5800.

0024-9297/91/2224-0252$02.50/0

ture of symmetric microphase-separated copolymers of polystyrene (PS) and poly(methyl methacrylate) (PMMA) was characterized by alternating layers of PS-rich and PMMA-rich phases. The PS-rich layer was located at the free surface and the PPMA-rich phase at the polymer substrate (silicon) interface.[13] The thickness of the surface layer was one-quarter that of the interlamellar spacing. For highly segregated systems, characterized by large $\chi N$ ($\chi$ is the Flory interaction parameter[9,10]), the layer adjacent to the free surface was a pure PS layer, and for systems of lower $\chi N$ this outer layer was a mixture of PS and PMMA.[14-19] $\psi_1$, the surface excess of PS, was shown to be well described by a $N^{-1/2}$ dependence.[19,20] We also showed that microscopic interactions between the unlike segments in the vicinity of the surface were modified[16,19] such that the surface ordered at a temperature above the bulk MST. In this paper we used XPS to determine the temperature dependence of the surface excess of PS for symmetric diblock copolymers of PS and PMMA. With the use of a model developed by Fredrickson,[11] we made estimates of the microscopic parameters that characterize the surface.

## Experimental Section

The PS–PMMA copolymers used in this study were all symmetric and exhibited lamellar morphologies in the bulk. Each was composed of $N$ segments, where $N$ ranged from 275 to 5244. Small-angle X-ray scattering (SAXS)[15] and neutron reflectivity[16] measurements showed that the interfacial thickness of each system was 50 ± 3 Å, independent of $N$. For the shortest copolymer the volume fraction occupied by the interface was approximately 60% at 170 °C. For the longest copolymer it was only ~10%. This clearly demonstrates that the copolymer systems vary from the weak to the strong segregation limit. The details of the copolymer systems have been discussed earlier.[15,19]

Details of the XPS experiments have been discussed previously [18-20] in a number of publications. The description here will therefore be brief. High-resolution XPS spectra were recorded by a Kratos XSAM 800 spectrometer by using a hemispherical analyzer with a high-resolution band-pass energy of 10 eV and detector slits of 5-mm width in a fixed retardation mode. A nonmonochromatized Mg K$\alpha$ radiation source of 300-W power produced X-rays of energy 1253.6 eV. The ultrahigh vacuum system had a base pressure of $7 \times 10^{-10}$ Torr. The calibration procedure used to determine the energy scale of the instrument has been discussed elsewhere.[20]

The PS–PMMA samples were solution cast onto a silicon wafer by using toluene as a solvent. The solvent was allowed to completely evaporate in vacuo. They were annealed in an ultraclean vacuum system at a pressure of $10^{-8}$ Torr. The samples were then allowed to return to room temperature before being transferred to the XPS analysis system. The high-resolution spectra of the O 1s and C 1s peaks were taken. These spectra are in quantitative agreement with those found in the literature.[20] Experiments were performed at different electron take-off angles, normal to the detector, where the deepest depth (~50 Å) was probed, and at take-off angles at 45°, 30°, and 20°. At 20° the shallowest depth was probed. Following satellite subtraction and background subtraction using the integral method of Shirley,[21] the peaks were fit with Gaussian line shapes with fwhm of 1.5 eV. During the analysis, care was taken to monitor both the peak shapes and the peak areas to check for radiation damage. During times in excess of the analysis, none was observed.

Two independent procedures were used to determine the surface excess of PS. One procedure was to utilize the fact that PS has no oxygen. The second was to note that the contribution of PS to the C 1s profile is twice that of PMMA. Both these procedures yielded results that were in excellent agreement with each other. This is shown in Table I for the shortest chain copolymer. Here the surface excess of PS is determined using the C 1s and O 1s peaks. It is also clear from this table that the composition shows a slight variation with the depth probed during the experiment. Further details of the experiment and analysis may be found in earlier publications.[18-20]

**Table I**

| $T$, °C | take-off angle, deg | $\psi_1$ (using O 1s) | $\psi_1$ (using C 1s) |
|---|---|---|---|
| 160 | 90 | 11 | 15 |
| | 40 | 10 | 9 |
| | 30 | 9 | 9 |
| | 20 | 10 | 9 |
| 170 | 90 | 23 | 22 |
| | 45 | 16 | 15 |
| | 30 | 14 | 15 |
| | 20 | 14 | 15 |
| 180 | 90 | 14 | 18 |
| | 40 | 13 | 12 |
| | 20 | 13 | 12 |

## Results and Discussion

In the calculation of bulk properties of large systems, it is often justified to ignore effects due to the surface on the bulk properties because the number of atoms close to the surface is very small in comparison to those in the bulk. Near critical points, however, where the correlation length, or order parameter, grows very large in magnitude, the surface and bulk properties are coupled. Under these conditions it is not reasonable to neglect the effects of the surface on the bulk properties.

The contribution of the surface to the bulk properties is addressed by adding to the bulk free energy a surface free energy term, $F_s[\psi]$, which is proportional to a surface energy density[11]

$$F_s(\psi) = [-H_1\psi(\mathbf{r}) + a_1\psi^2(\mathbf{r})/2]/N \qquad (1)$$

$\psi(\mathbf{r})$ is the order parameter

$$\psi(\mathbf{r}) = \langle\rho_A(\mathbf{r})\rangle/\rho - f \qquad (2)$$

It is the local deviation of the A-component density, of an A–B diblock system, from its average bulk value ($\rho = \langle\rho_A(\mathbf{r})\rangle + \langle\rho_B(\mathbf{r})\rangle$). $H_1$ and $a_1$ are phenomenological parameters that describe the effects of the surface on the bulk thermodynamic potential. Both $H_1$ and $a_1$ are defined such that they are proportional to $N$.[11] $H_1$ is a "field" that may be related to a chemical potential, or surface energy difference, that favors the A-component at the surface; it is assumed to be small. The parameter $a_1$ describes the way in which the surface potential modifies the interactions between the molecules in the near surface region. It can have values that are positive, negative, or zero. An indication of the physical significance of this parameter can obtained by considering the case where the "field", $H_1$, is zero. If $a_1 \geq 0$, the surface energy is increased (cf. eq 1) by having an A-component-rich layer at the surface. Therefore, an excess of the A component, the lower surface energy component, at the surface is unlikely under these conditions. An alternate way of thinking about this is that the local interaction parameter in the vicinity of the surface, $\chi_{\mathrm{local}}$, is less than that of the bulk, $\chi_{\mathrm{bulk}}$. For a negative $a_1$, the surface energy is decreased by having a A-component-rich layer at the surface. This would be independent of whether the bulk is disordered or not. Consequently, the ordering of a disordered block copolymer system would always occur at the surface. For $a_1 = 0$, the surface and bulk order spontaneously in the absence of the field. In the case of a nonzero field, an A-rich surface layer is possible with a positive $a_1$.

There are analogies between polymer surfaces and Ising ferromagnetics.[22] In surface critical behavior of some systems that exhibit magnetic order, it is customary to refer to a surface extrapolation length, $\lambda$.[22] In the case of

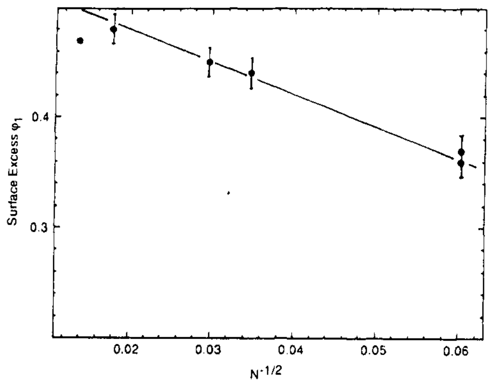

**Figure 1.** Surface excess of polystyrene, $\psi_1$, as a function of $N^{-1/2}$ at 180 °C.

polymer surfaces $\lambda = B/a_1$, where $B^{1/2} \sim N^{1/2}$ is a measure of the range of interactions between the molecules in the system. Physically, $\lambda$ represents the depth of the region beneath the surface where effects due to the surface potential are important. $\lambda$ should be on the order of a statistical segment length. It effectively yields the same information as $a_1$.

The surface excess of the more surface-active species is given by

$$\psi_1 = \left[\frac{8\bar{\chi}_s\epsilon}{\Delta}\right]^{1/2} Q_1 \cos\phi \qquad (3)$$

where $Q_1$ is a surface amplitude given by

$$Q_1 = \left[\frac{1}{2}(\gamma \tan\phi + \xi_-/\lambda)^2 + \frac{H_1\xi_-}{B\cos\phi}\left(\frac{\Delta}{4\bar{\chi}_s\epsilon}\right)^{1/2} + 1\right]^{1/2} - \frac{1}{2^{1/2}}(\gamma\tan\phi + \xi_-/\lambda)$$

The correlation length is $\xi_- = (4B/\epsilon\bar{\chi}_s)^{1/2}$. $\Delta$ is a coefficient which has a value of 157 for $f = {}^1/_2$. $\epsilon$ describes the proximity of the system to the MST. It is given by $\epsilon = (\bar{\chi} - \bar{\chi}_s)/\bar{\chi}_s$, where $\bar{\chi}_s = 3^{1/2}/[f(1-f)]^{3/2}$ and $\bar{\chi}$ is related to the normal Flory interaction parameter, $\chi$, by $\bar{\chi} = 2\chi N - 2(\chi N)_s + 3^{1/2}/[f(1-f)]^{3/2}$. Here, $(\chi N)_s$ is the value of $\chi N$ at the spinodal. In this formalism it is assumed that $\epsilon$ is very small ($0 < \epsilon \ll 1$), i.e., near the MST. $\gamma$ is given by $(2/\epsilon)^{1/2}$, and $\phi$ is a phase angle, which at the critical point is zero.

It is possible to determine experimentally the parameters that characterize the surface. Using XPS, one can obtain the surface excess as a function of $N$. An explicit $N$ dependent for $\psi_1$ may be obtained from the above equations by performing an expansion of eq 3 and noting that $\epsilon$ is very small (weak segregation limit; $\tan\phi \sim \epsilon^{1/2}$ and $\cos\phi \approx 1$)[11] and that $H_1 < N^{3/2}$. One gets for the surface excess of PS (the more surface active species) the result that [18,19]

$$\psi_1 \approx \frac{H_1\lambda}{B} - 2.7\left(\frac{H_1\lambda}{B}\right)^2 \lambda N^{-1/2} \qquad (4)$$

Terms of order $1/N$ are ignored. The data in Figure 1 show that the surface excess of PS is well described by a $N^{-1/2}$ dependence at 180 °C. In an earlier paper,[19] we showed similar results at 170 °C (it may be emphasized that under nonequilibrium conditions the surface excess varies considerably from that shown here). It is clear from this data that in the strong segregation limit the surface excess is $\psi_1 = 0.5$ (pure PS) and for the weakly segregated systems it varies as $N^{-1/2}$. This $N$ dependence arises from the fact that the correlation length $\sim B^{1/2} \sim N^{1/2}$. It is independent of the proximity of the system to the MST. Equation 4, however, is simple and enables the determination of the microscopic parameters, $H_1$, $a_1$, and $\lambda$, that characterize the surface properties. Later a self-consistent check, using these parameters, is made in order to verify that the above approximations are reasonable.

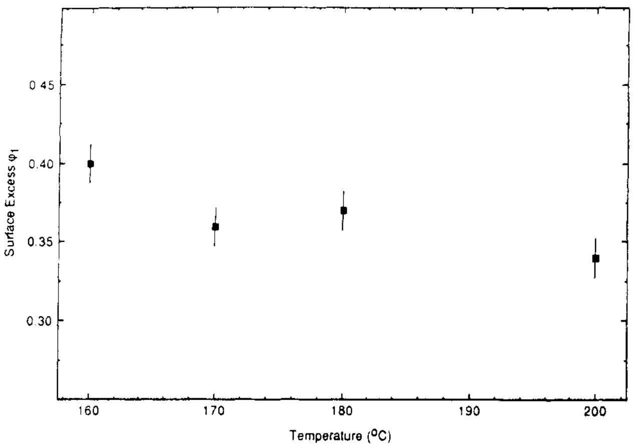

**Figure 2.** Surface excess of the shortest copolymer chain ($N$ = 275) as a function of temperature. The data plotted here are for the shallowest depths probed where the surface excess obtained is largest (the value of the surface excess at 170 °C is slightly smaller than that reported in ref 20).

We now restrict our attention to the sample in the weakly segregated regime where the theory is meant to apply. When eq 4 and our experimental data, Figure 1, are used the parameters $H_1$, $a_1$, and $\lambda$ may be calculated by noting that as $N$ approaches inifinity $\psi_1$ has to approach a constant value of $H_1\lambda/B = 0.5$, a pure layer of PS. It follows that $\lambda \approx 3$ at this temperature. This value of $\lambda$ is entirely reasonable since $\lambda$ should be on the order of a few statistical segment lengths. In units of statistical segment length, $b$, $a_1$ has a value of 29. It can be converted to units of energy per unit area by multiplying by the factor $k_BT/b^3$, where $k_B$ is the Boltzmann factor and $T$ is the absolute temperature. The "field" $H_1 = 14.5$. The surface energy can be calculated by using eq 1 to show that it is less than 1 mJ/m$^2$, which is consistent with the reported surface energy difference between the components.[23] It should be emphasized here that a positive $\lambda$ ($a_1 > 0$) does not imply that $\chi_{\text{local}} < \chi_{\text{bulk}}$. The "field" is nonzero and positive. With this positive $H_1$ the surface energy is decreased by always having a PS-rich layer at the surface ($\psi_1 > 0$). Therefore, one should always expect ordering to begin at the surface. This is the underlining reason for the direct observations concerning the PS-$d$/PMMA system reported in ref 16 where ordering began at the surface and induced ordering in the bulk. This points to an interesting conclusion that, for copolymer mixtures in the vicinity of an interface, where one component exhibits an affinity for the interface ($H_1 > 0$), the ordering process should always begin at that interface. This is observed in all the surface-related measurements involving SIMS and neutron reflectivity.

Figure 2 shows a plot of the surface excess as a function of temperature for the $N$ = 275 segment copolymer. The data in these figures represent the surface excess determined at electron take-off angles of 20°. The surface excess of PS decreases with increasing $T$. The "field" $H_1$ also decreases with increasing temperature, as seen in Figure 3 where $H_1/N$ (in units $b$) is plotted as a function of $T$.

Having extracted values for $\lambda$ and $H_1$ at different temperatures, we may use eq 3 to determine $\epsilon$, the proximity of the system to the MST, and hence $\chi$. The

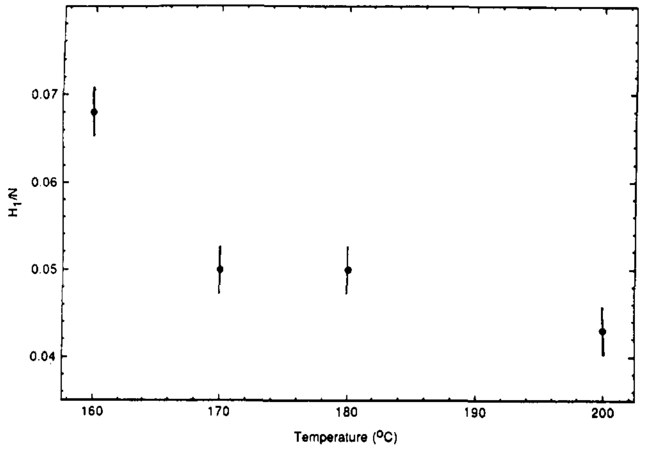

**Figure 3.** Plot of $H_1/N$ as a function of temperature.

result will provide a self-consistent check for the approximations made. Though $\lambda$ and $H_1$ were obtained by using eq 4, which is an expansion of eq 3, their values should be very close to being exact since the contribution of the terms of order $1/N$ in eq 4 are significant. Bearing this in mind, we can then use eq 3 to calculate $\epsilon$. Assuming, as we did earlier, that, for very small $\epsilon$, $\tan \phi \sim \epsilon^{1/2}$ and $\cos \phi \approx 1$, we obtained $\epsilon = 0.05$ ($\chi > \chi_s$) and $\chi = 0.0397$ at 180 °C. The fact that $\epsilon$ is not only very small but of the correct sign is a strong indication that our approximations are reasonable. The value of $\chi$ extracted is also reasonable since it is slightly larger than that found for the PS-*d*/PMMA system ($\chi = 0.0367$),[24] which is slightly more compatible.

## Conclusion

We have shown that in a highly segregated symmetric diblock copolymer system the surface is comprised of only the lower surface energy component. For systems that are weakly segregated, the surface layer is a mixture of both components. Using mean-field theory and the experimental data, it is shown that the microscopic interactions in the vicinity of the surface are modified such that there should always be a PS-rich layer at the surface. Hence, the near surface region should always induce ordering in the bulk. The surface excess and the chemical potential difference $H_1$ that favors the lower surface energy component both decrease systematically with increasing temperature. Estimates of $\epsilon$, the proximity of the copolymer system of the MST, provided a self-consistent check that the approximations we made were reasonable.

**Acknowledgment.** This work performed at Sandia National Laboratories, was supported by the U.S. Department of Energy under Contract No. DE-AC04-76DP00789.

## References and Notes

(1) Goodman, I., Ed. *Developments in Block Copolymers*; Applied Science: New York, 1982.
(2) Leibler, L.; *Macromolecules* **1980**, *13*, 1602.
(3) Ohta, T.; Kawasaki, K. *Macrmolecules* **1986**, *19*, 2621. Semenov, A. N. *Sov. Phys.-JETP* **1985**, *61*, 733.
(4) Blakley, J. M. In *Chemistry and Physics of Solid Surfaces*; Vanselow, R., Ed.; CRC Press: Boca Raton, FL, 1979; Vol. 2.
(5) Rostogi, A. K.; St. Pierre, L. E. *J. Colloid Interface Sci.* **1969**, *31*, 168.
(6) Schmitt, R. L.; Gardella, J. A., Jr.; Magill, J. H.; Salvati, L., Jr.; Chin, R. L. *Macromolecules* **1985**, *18*, 2675.
(7) Thomas, H. R.; O'Malley, J. J. *Macromolecules* **1979**, *12*, 323.
(8) Hasegawa, H.; Hashimoto, T. *Macromolecules* **1985**, *18*, 589.
(9) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953.
(10) de Gennes, P.-G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979.
(11) Fredrickson, G. H. *Macromolecules* **1987**, *20*, 2535.
(12) Jones, R. A. L.; Kramer, E. J.; Rafailovich, M. H.; Sokolov, J.; Schwarz, S. A. *Phys. Rev. Lett.* **1989**, *62*, 280.
(13) Coulon, G.; Russell, T. P.; Deline, V. R.; Green, P. F. *Macromolecules* **1989**, *22*, 2581.
(14) Green, P. F.; Russell, T. P.; Jerome, R.; Granville, M. *Macromolecules* **1989**, *22*, 908.
(15) Anastasiadis, S. H.; Russell, T. P.; Satija, S. K.; Majkrzak, C. F. *J. Chem. Phys.* **1990**, *92*, 5677.
(16) Anastasiadis, S. H.; Russell, T. P.; Satija, S. K.; Majkzrak, C. K. *Phys. Rev. Lett.* **1989**, *62*, 1852.
(17) Green, P. F.; Christensen, T. M.; Anastasiadis, S. H.; Russell, T. P. *Proceedings of the Materials Research Society* **1990**, *171*, 317.
(18) Green, F.; Christensen, T. M.; Russell, T. P.; Jerome, R. *Macromolecules* **1989**, *22*, 2189.
(19) Green, P. F.; Christensen, T. M.; Russell, T. P.; Jerome, R. *J. Chem. Phys.* **1990**, *92* (2), 1478.
(20) Clark, D. T.; Peeling, J.; O'Malley, J. M. *J. Polym. Sci., Polym. Chem. Ed.* **1976**, *14*, 543. Clark, D. T.; Thomas, H. R. *J. Polym. Sci.* **1978**, *16*, 791.
(21) Shirley, D. A. *Phys. Rev. B*, **1972**, *5*, 4709.
(22) Binder, K. In *Phase Transitions and Critical Phenomena*; Domb, C., Lebowitz, J. L., Eds.; Academic Press: New York, 1983; Vol. 8.
(23) Wu, S. *Polymer Interfaces and Adhesion*; Marcel Dekker: New York, 1982; p 73.
(24) Russell, T. P.; Seeger, P.; Hjelm, R. P. *Macromolecules* **1990**, *23*, 890.

**Registry No.** (PS)(PMMA) (block copolymer), 106911-77-7.