

Entropy-Driven Surface Segregation in Block Copolymer Melts

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(Received 17 June 1992)

Surface segregation in thin films of symmetric polyolefin diblock copolymers containing a lamellar microstructure, cast on a variety of substrates, has been investigated. In all cases, the conformationally smaller block preferentially segregated to both the solid and air interfaces even though the surface energy of the solid substrate always exceeded that of the block copolymer. These results indicate an entropically driven surface segregation effect that we attribute to block conformational asymmetry.

PACS numbers: 61.12.Ex, 61.41.+e, 68.10.Cr, 68.65.+g

Practical uses of condensed matter are frequently dictated by physical and chemical interactions that occur within the first few nanometers of a surface. Adhesion, lubrication, wetting, catalysis, corrosion, and thrombosis in medical implants are just several among many processes that depend directly on surface composition and structure. Thus, our ability to control and tailor surfaces is closely linked to advances in interfacial science and engineering.

Surface activity, or wetting, in polymer mixtures can generally be anticipated based on the difference in surface tension between the pure components and the substrate. An elegant example is the segregation of deuterated polystyrene to an air interface from a mixture with normal (protonated) polystyrene [1]. This effect is explainable based on the slightly lower cohesive energy density that characterizes the heavier isotope [2]. Analogously, segregation to a solid surface will occur when the wetting component provides the lowest interfacial tension, or exhibits a specific (e.g., chemical) affinity for the substrate. For example, Anastasiadis *et al.* [3] have demonstrated that diblock copolymers of polystyrene (PS) and polymethylmethacrylate (PMMA) containing equal-molecular-weight PS and PMMA blocks ($f = \frac{1}{2}$) form periodic lamellar microstructured thin films with a PMMA layer making exclusive contact with the SiO₂ substrate (native oxide layer on Si) while a PS layer forms the film-air interface. This result, referred to as an asymmetric film as illustrated in Fig. 1(a), can be rationalized [4] based on the selective chemisorption of PMMA to metal oxides and a lower surface tension for PS. However, if the SiO₂ substrate is replaced by gold, PS is reported [5] to segregate to both the film-air and film-solid interface, forming the symmetric film structure depicted in Fig. 1(b). This behavior can be understood based on the observation that aromatic hydrocarbons exhibit higher heats of adsorption on gold than aliphatic hydrocarbons [6]. If the polymethylmethacrylate block is replaced by polybutylmethacrylate (PBMA), a symmetric structure is again observed [7] with the PBMA segregating to the air and SiO₂ interfaces. In this instance the

butyl group reduces the surface tension of PBMA below that of PS [8] without significantly disturbing its chemical affinity for SiO₂. In the examples outlined above, and all others we are aware of [9], surface segregation in polymer-polymer systems containing roughly equal-molecular-weight components (or blocks) is governed by enthalpic factors.

Recently, we found an exception to this behavior [10]. A model polyolefin block copolymer, $f \cong 0.5$ poly(ethylene-propylene)-poly(ethylene) (PEP-PEE), produced symmetric thin films where PEE is the surface-active species, without an apparent enthalpic driving force. Because PEP and PEE are simple saturated hydrocarbons there is little difference in the purely van der

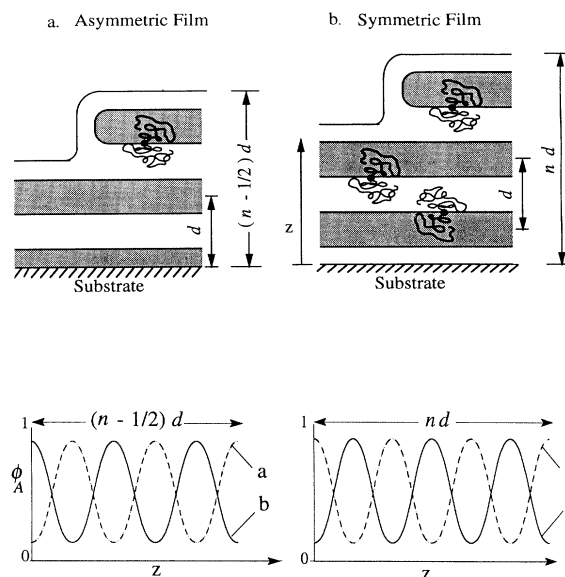


FIG. 1. Possible thin-film geometries for symmetric ($f=0.5$) diblock copolymers, where d is the lamellar period and n is an integer: (a) enrichment of different blocks at the air and substrate interfaces, and (b) enrichment of the same block at both interfaces. Each type of film can have two different composition profiles, phase shifted by 180°.

Waal's interactions to produce preferential surface segregation. Furthermore, small variations in surface energy (ca. 1–2 dyn/cm [11]) could not account for segregation of PEE to *both* the higher and lower energy interface in the absence of a specific chemical interaction. We are unable to identify any specific interaction that would discriminate between these chemical isomers. In this Letter we report experimental results that indicate that an entropic driving force is responsible for such segregation, in qualitative agreement with recent theory. This finding reveals a new approach for manipulating the surface composition block copolymers and polymer mixtures.

Three model polyolefin diblock copolymers were used in this study. The principal molecular structure, density, and statistical segment length, a ($a^2 = 6R_g^2/N$, where R_g and N are the unperturbed radius of gyration and the degree of polymerization, respectively) for the polymer blocks are listed in Table I. PEP-PEE, PE-PEE, and PE-PEP specimens with $f \approx \frac{1}{2}$ were synthesized and characterized using established procedures [12]. In each case, deuterated monomer was used in preparing one of the blocks in order to introduce neutron contrast. The degree of polymerization, isotope content, composition, order-disorder transition temperature (T_{ODT}), and bulk lamellar spacing d are presented in Table II. Methods for obtaining T_{ODT} and d have been described in earlier publications [13].

Thin films of these materials were prepared by spin coating from solution [14] onto either 2- or 4-in.-diam flat substrates. Silicon surfaces were produced by stripping the native oxide layer from wafers using an HF solution followed by rinsing and immediate spin coating [15]. Smooth polystyrene substrates were generated by spin coating this polymer onto silicon wafers; uniformity and flatness were confirmed by x-ray reflection measurements. Silver surfaces were obtained by evaporating the metal onto Si wafers. Polished optical quartz disks were used as received.

Lamellar block copolymers can assume four distinct thin-film geometries as illustrated in Fig. 1: symmetric or asymmetric with either the A or B block situated at the polymer-substrate interface. In addition, the deposition

TABLE I. Model polyolefin molecular characteristics [22].

Polyolefin	Chemical Structure	ρ , g/cm ³		a , Å	
		23°	130°C	23°	130°C
PE (polyethylene)	$-\left[CH_2-CH_2-CH_2-CH_2\right]_N-$	--	0.79	--	8.3
PEP (polyethylene-propylene)	$-\left[CH_2-\overset{CH_3}{CH}-CH_2-CH_2\right]_N-$	0.85	0.79	7.2	6.8
PEE (polyethylethylene)	$-\left[CH_2-\underset{\begin{array}{c} CH_2 \\ \\ CH_3 \end{array}}{CH}\right]_N-$	0.87	0.81	5.0	5.1

^aBased on a segment volume of 1.17×10^{-22} cm³.

TABLE II. Polyolefin block copolymers.

$A-B$ diblock copolymer	$10^3 N^a$	f_A	T_{ODT} (°C)	Bulk lamellar period d (Å)
PEP-PEE(d_6)	0.96	0.55	125	341
PE(d_6)-PEE	0.47	0.53	180	246
PE(d_6)-PEP	2.0	0.50	138	534

^aBased on a segment volume of 1.17×10^{-22} cm³.

of non-integral or non-half-integral amounts of material [$\langle t \rangle \neq dn$ or $\langle t \rangle \neq d(n - \frac{1}{2})$] for the symmetric and asymmetric cases, respectively, where $\langle t \rangle$ is the average film thickness and n is a positive integer] leads to a surface topology composed of islands or holes of thickness d . These defects are easily observed by phase contrast interference microscopy as described by Coulon *et al.* [16]. Measurements of $\langle t \rangle$ (± 5 Å) by x-ray reflection [17] and spectroscopic ellipsometry on relatively uniform (i.e., defect-free) films conclusively demonstrated that each of our polyolefin diblock copolymers forms the *symmetric* lamellar geometry where $\langle t \rangle \cong nd$ based on d values that were obtained from bulk specimens by small-angle neutron scattering (Table II). This result is further substantiated by neutron reflection experiments as described below. Phase contrast interference microscopy (Zygo microscope) also confirmed that when $\langle t \rangle \neq nd$ nonintegral amounts of polymer resulted in the formation of holes and islands of thickness d as illustrated in Fig. 1(b).

Determination of the phase (i.e., the surface-active block) of the composition profiles was accomplished using neutron reflectivity measurements, performed with the fixed-wavelength ($\lambda = 2.35$ Å) reflectometer at beam line seven in the reactor hall of the National Institute of Standards and Technology. Measurements were made on relatively defect-free films ($\langle t \rangle \cong nd$) at room temperature (PEP-PEE) and 130°C (PE-PEE and PE-PEP), the latter being above the melting temperature of PE, $T_{m,PE} = 108$ °C. The high-temperature experiments were conducted using a vacuum sample chamber to guard against oxidative degradation. A detailed discussion of the experimental techniques used can be found elsewhere [10]. The composition at the polymer-air interface was also determined for several specimens of each material by static secondary ion mass spectrometry (SIMS) and was found to agree within experimental error with the neutron reflection analysis.

Representative neutron reflectivity data for each of the three polyolefin diblock copolymers are shown (open circles) in Fig. 2 along with the optimized fits (solid curves). Since we are primarily concerned with establishing the phase, and not the detailed shape of the composition profiles, only the qualitative results are currently presented. However, because all three materials are relatively close to the order-disorder transition temperature (Table II), the associated composition profiles closely resemble

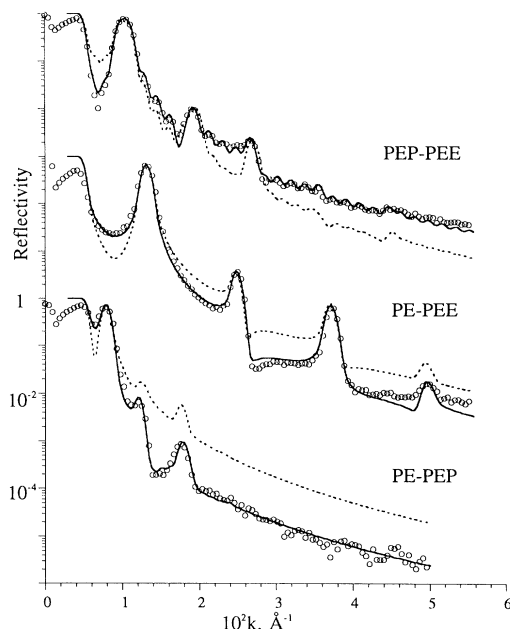


FIG. 2. Experimental neutron reflectivity data (open symbols) for representative polyolefin diblock copolymer films listed in Table III. Data for films cast on etched single-crystal silicon are shown along with calculated fits for optimized composition profiles (solid curves) and profiles phase shifted by 180° (dashed curves). Progressive vertical shifts of three orders of magnitude have been applied to the plots labeled PE-PEE and PEP-PEE. Lack of agreement between the calculated and measured reflectivities below the critical wave vector, $k_c = 0.005 \text{ \AA}^{-1}$, is an experimental artifact [10].

those reported earlier for PEP-PEE specimens near T_{ODT} [10]. (Here we note that this proximity to T_{ODT} insures that the films achieve an equilibrium state.) Also shown by the dashed curves are the reflectivities associated with the optimized composition profile when phase shifted 180° [see Fig. 1(b)].

The fitting procedure for both symmetric composition profiles involved using a Fourier series [18] representation of the profile, where the magnitude of the coefficients controls the intensity and shape of the Bragg peaks in the calculated resonance. The first of the coefficients is invariant with respect to phase and dictated by the amplitude of the composition profile. For this reason the peak intensity of the first Bragg reflection is not affected by changing the phase. However, the shape and intensity of higher-order reflections are dependent on phase. This derives from the relative contributions of the sine and cosine components for these reflections which cannot be equivalent for both phase types on a finite-sized symmetric profile. Following these guidelines, we began by fitting the position and amplitude of the first Bragg peak for both phase types. Then the position, amplitude, and shape of the higher-order reflections were fitted by the choice of appropriate Fourier terms. In all cases, we were unable to reduce the phase-shifted profiles (dashed

TABLE III. Thin film characteristics. d is the lamellar period, n is the number of bilayers, and ϕ_s is the surface concentration.

Diblock copolymer	Substrate	d (\AA)	n	Surface block	ϕ_s
PEP-PEE(d_6)	Si ^a	348 ± 5	5	PEE(d_6)	0.90
	Polystyrene	330	3	PEE(d_6)	0.87
	Ag	325	5	PEE(d_6)	0.83
	Quartz	330	5	PEE(d_6)	0.87
PE(d_6)-PEE	Si ^a	255	12	PEE	0.87
PE(d_6)-PEP	Si ^a	535	6	PEP	0.72

^aStripped with a 10% aqueous HF solution.

curves) to satisfactory fits. Although not shown, neither asymmetric composition profile [Fig. 1(a)] could be brought into satisfactory agreement with the neutron reflection data, in agreement with our conclusions based on x-ray reflection and ellipsometric measurements.

The type and volume fraction ϕ_s of the surface-active block for the PEP-PEE, PE-PEE, and PE-PEP diblock copolymers are listed in Table III, along with the measured lamellar periods which are in close agreement with the bulk values (Table II). Surface segregation does not depend on the surface energy of the solid substrate as evidenced by the neutron reflection results obtained from PEP-PEE on silicon, polystyrene, quartz, and silver [19] (see Table III). Nor is surface activity correlated with the isotope content of the surface-active block; i.e., the deuterated PEE block in PEP-PEE (d_6) appears at both surfaces while the PEP block in PE(d_6)-PEP is driven to the film boundaries. However, in every instance the block with the shorter statistical segment length segregates to both film interfaces (Tables I and III).

We believe these results can be explained by arguments offered in a recent paper by Fredrickson and Donley [20]. They construct an excess surface free-energy expression for an incompressible binary blend of homopolymers in the vicinity of a hard wall. When the decay length of the concentration profile is long compared with the radii of gyration of both chains, their surface free-energy expression reduces to

$$\mathcal{F}_s[\phi] = -\frac{1}{2}(a_A^2 - a_B^2)\phi_1 - \mu_1\phi_1 - \frac{1}{2}g\phi_1^2, \quad (1)$$

where a_A and a_B are the statistical segment lengths of A and B components and ϕ_1 and $\dot{\phi}_1$ are the surface concentration and its gradient, respectively. μ_1 and g are, respectively, a surface chemical potential describing the energetic preference of the surface for one of the species and a parameter that describes the modification of the A - B interactions (i.e., the segment-segment interaction parameter χ) due to the surface.

The first term in Eq. (1), which is not accounted for in previous investigations of wetting in polymer mixtures, arises from the unequal conformational perturbation experienced by the two chain types in the presence of an impenetrable surface. When $a_A = a_B$, this entropic penal-

ty becomes symmetric and Eq. (1) reduces to the conventional form [21]. Otherwise, Eq. (1) tends to favor an excess of the more flexible component in the surface layer. To demonstrate this, imagine that species A is more flexible than species B , i.e., $a_A < a_B$. The coefficient of ϕ_1 is then positive, which means that the free energy is a minimum when the concentration profile $\phi(z) = \phi_A(z)$ has a negative slope at the surface ($\phi_1 < 0$). This corresponds to a surface excess of species A , the component with the smaller statistical segment length.

In general, the selection of the surface wetting component will be dictated by a combination of the entropic factors embodied in the first term of Eq. (1) and enthalpic factors included in μ_1 . A large difference in surface energies between the two components will cause the low-surface-energy species to enrich the free surface. Similarly, a difference in polymer-solid interaction energy will cause the species that lowers the interfacial tension to segregate to the solid surface. If the differences in surface energies are small, then the difference in statistical segment lengths can drive the more flexible component to the surface. We believe the polyolefin block copolymers described in this Letter belong to the second category of materials.

These theoretical arguments have been constructed for a homopolymer blend in the vicinity of a hard wall. Nevertheless, we believe that similar arguments will apply to block copolymers since surface selectivity derives from differences in the local chain flexibility and not the overall chain dimensions. However, there is a significant experimental advantage in working with block copolymers since lateral phase separation is precluded.

In summary, we have presented results that indicate entropy-driven surface segregation in polyolefin diblock copolymer melts. This phenomenon, which leads to symmetric film formation, is attributed to diblock copolymer conformational asymmetry. We envision a variety of possible applications for this result, where control over surface composition is important. For example, small amounts of block copolymer, possibly containing specific functional groups, could be added to a bulk material and driven to the surfaces based on tailored conformational dimensions. More complex molecular structures, such as triblock or starblock architectures, may enhance these effects.

This research was supported by the NSF under a Presidential Young Investigator Grant to F.S.B. (No. DMR-8957386) and by the Center for Interfacial Engineering (CIE), an engineering research center at the University of Minnesota.

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