Surface Composition of Amorphous and Crystallizable Polyethylene Blends As Measured by Static SIMS

P. Brant,*,[†] A. Karim,*,[‡] J. F. Douglas,[‡] and F. S. Bates[§]

Baytown Polymers Center, Exxon Chemical Company, Baytown, Texas 77522, Polymers Division, NIST, Gaithersburg, Maryland 20899, and Department of Chemical Engineering and Material Science, University of Minnesota, Minneapolis, Minnesota 55455

Received September 8, 1995; Revised Manuscript Received May 30, 1996[⊗]

ABSTRACT: The surface composition of several thin-film semicrystalline polyolefin blends is quantified using secondary ion mass spectroscopy (SIMS). These experiments indicate that the component having the lower crystallinity migrates to the free surface so that the degree of crystallinity is an important factor along with the local polymer−polymer interaction and chain stiffness in determining the surface segregation in polymer blends. Specifically, a systematic study involving mixtures of amorphous polymers [poly(ethylethylene) (PEE), poly(ethylenepropylene) (PEP), and poly(ethylene-*co*-(1-dodecene)) (EC12)] with semicrystalline model polyethylenes (PE) having various densities (crystalline content) showed the greatest degree of surface enrichment for the amorphous polymers PEE and EC12 and to a lesser degree PEP. The degree of surface segregation for the PE materials, was higher for the lower density materials which have a higher amorphous content. Surface enrichment of amorphous component as high as 50-fold was observed. SIMS measurements thus show a definite heirarchy in the degree of surface enrichment according to the degree of crystallinity as well as the relative chain stiffness of the blend components in these model polymer systems.

1. Introduction

Commercially important films often either intentionally or unintentionally involve polymer blends which have one or more semicrystalline or amorphous components. Molecular parameters such as molecular weight, chain architecture, and the degree of crystallinity are all important in controlling the material properties of these films. While the bulk properties of crystalline−amorphous polyolefin blends have been extensively studied,[1] there are few studies of the surface properties of these blend films. These surface properties substantially affect the performance of thin films in applications.

The composition of blends near surfaces can be markedly different from the bulk composition,[2−8] and a variety of factors can influence this tendency toward surface segregation. Of course, an unfavorable enthalpic interaction leads to a strong tendency for blends to stratify transverse to the interface and to form composition modulations in the plane of the film. The blend component having the lower surface tension is usually found to migrate to the surface. For example, small quantities ($\leq 1\%$) of a very low surface tension polymer, such as poly(dimethylsiloxane) ($\gamma \approx 0.021$ N/m) blended with a hydrocarbon polymer ($\gamma \approx 0.029{-}0.034$ N/m), results in almost full coverage of the surface by the low surface tension polymer. More subtle factors come into play in nearly miscible blends, however.[9] Recently, it has been shown[10−12] that differences in chain flexibility can give rise to a systematic tendency of the more flexible block to migrate to the free boundary of block copolymer lamellae films. Sikka et al.[10a] propose that this effect arises from differences in chain entropy associated with differences in the relative flexibilities of the polymers. Klein et al.[13] and others[12] have also shown that surface segregation in amorphous polyolefin blend films can be sensitive to small variations in chain architecture, and they likewise attribute their observations to the different flexibilities of the components of their polyolefin blends. Heuristically, we anticipate that the degree of crystallinity of the blend components can likewise influence the entropy of the polymer blend component near the free boundary and thus provide a selecting factor when enthalpic and flexibility factors do not predominate.[10b] The present work systematically examines this possibility.

In the present paper, we find that when a blend is comprised of two polyolefins of different crystallinity, but matched in molecular weight and molecular weight distribution (MWD), the top surface (≤ 20 Å) of the blend is indeed enriched in the less crystalline component.[14] The semicrystalline component is rejected from the surface altogether in extreme cases. Selected experiments were also carried out on binary blends of amorphous polymers to check the validity of our technique on previously studied systems and as a "control" for our other studies on semicrystalline polymer blends.

2. Experimental Section

Table 1 lists some of the physical properties of the polymers used to prepare the various blends. For this study, we have used the following amorphous polymers: poly(ethylethylene) [PEE is a model amorphous poly(1-butene)], poly(ethylenepropylene) [PEP is a model ethylenepropylene (EP) rubber], poly(ethylene-*co*-dodecene) (EC12, 29.4 mol % 1-C_{12}), and poly(1-decene) [h-(1-C_{10})$_x$]. The partially deuterated PEE polymers listed in Table 1 were random copolymers used for calibration purposes. The model semicrystalline polymers were high-density polyethylene (both narrow and broad MWD HDPE), medium-density polyethylene (MDPE), and hydrogenated 1,4-polybutadiene, which is often considered to be a model linear low-density polyethylene (LLDPE). Thus, the crystallinity of the components was varied from zero (amorphous) to about 65% (HDPE). In many blends, the polymer molecular weights and molecular weight distributions were approximately matched (all MWD polydispersity indices (α) are in the range 1.1−2.1 with the exception of the broad molecular weight distribution (BMWD) HDPE, where $\alpha \approx 35$). Films were also prepared containing two crystallizable components where the crystallinity of one component is markedly different from the other.

---

* Authors to whom correspondence should be addressed.

[†] Exxon Chemical Co.

[‡] NIST.

[§] University of Minnesota.

[⊗] Abstract published in *Advance ACS Abstracts,* July 15, 1996.

S0024-9297(95)01349-0 CCC: $12.00

Table 1. Properties of Polymers Used in Thin-Film Blends

polymer	mol % D	$M_w \times 10^3$	MWD	mp, °C	density, g/cm^3
d-HDPE[a]	100	108	1.8	130	1.095
d-LLPDE	100	160	1.1	108	1.045
HDPE BMWD	0	200	35	132	0.950
HDPE NMWD	0	144	1.97	126	0.956
MDPE	0	61	2.0	118	0.924
d-PEE (poly(ethylethylene))	100	160	1.1		0.886
d-PEP (poly(ethylenepropylene))	100	155	1.1		0.886
h-PEP (poly(ethylene-propylene))	0	155	1.1		0.857
h-(1-C$_{10}$)$_x$ (poly(1-decene))	0	5	2		0.857
EC12 (poly(ethylene-*co*-dodecene))[b]	0	94	2.0		0.857
PEE -73 (poly(ethylethylene))	25	11.5	1.05		0.870
PEE-90 (poly(ethylethylene))	76	11.5	1.05		0.880

[a] Provided courtesy of F. C. Stehling. [b] 29.4 mol % 1-dodecene.

In two cases, blends containing two amorphous polymers were also examined. Films made from one amorphous and one crystallizable polymer had compositions ranging from 2 to 50 wt % amorphous polymer. Blends made from two crystallizable polymers or two amorphous polymers had 50:50 by mass compositions. In each case, one component of the blend was fully deuterated to distinguish it from the other component. In several of the blends, the crystallizable polymer was the deuterated component. It was important to change the roles of the deuterated component in several instances to ensure that the deuteration[9] was not itself substantially influencing the results. As-cast and annealed films were examined by static secondary ion mass spectrometry (SIMS), a powerful technique for probing surface compositions.[15,16]

The amorphous polymers and blend films were prepared by either spin casting the polymer from its solution in *o*-xylene solution at a rotation speed of 2000 rpm or by statically casting onto silicon wafers from polymerization grade toluene solutions and dried under nitrogen. It was verified that the different casting procedures did not affect the static SIMS spectra in any way. In cases where one or more components are semicrystalline, spin casting was performed using a hot (~90 °C) solution of the components to be cast and the silicon wafer was preheated to ≈90 °C as well. In some cases, thin films were analyzed "as cast". More often, films were annealed under vacuum at 140 °C for 10 h and then cooled to ambient temperature under vacuum before analysis. Attempts were made to measure film thicknesses of the spin-cast films containing semicrystalline polymers using a Gaertner variable-angle ellipsometer.[17] However, the ellipsometric measurements made at different angles did not converge to a single thickness. Film thicknesses (≈1000 Å) were accurately measured on selected films by neutron reflectivity at the National Institute of Standards and Technology in Gaithersburg, MD. Neutron reflectivity measurements on these films will be reported separately.

Static SIMS measurements were conducted on Charles Evans and Associates instruments at two separate locations. Static SIMS measurements were carried out at Charles Evans Associates in Minnesota using a Physical Electronics 5700 Multitechnique spectrometer equipped with a dual-pass quadrupole mass spectrometer. Spectra were generated using a 7 keV Xe$^+$ ion beam (0.15 nA). The beam was rastered over an area 4 × 4 mm^2. A base vacuum of 1×10^{-8} Pa was reached within 10 min of sample insertion. Data collection was complete within 2.4 min. Total [primary ions/cm^2] dose for the spectra recorded ranges between 3×10^{12} and 5×10^{12}. Thus, spectra were all collected at or below the so-called "static limit" (~5 x 10^{12} ions/cm^2) first described by Benninghoven.[18] Selection of specific areas could be made by viewing the surface through an in-situ low-magnification scanning electron microscope. Measurements were often made on more than one area to ensure homogeneity of surface composition and on identically prepared samples to ensure reproducibility of results. Nominal spectral variations were noted between the different measurements. In some cases, the samples were charged relative to instrument ground. This charging is routinely neutralized by a low-energy electron beam. No evidence of residual solvent was found in any of the spectra recorded.

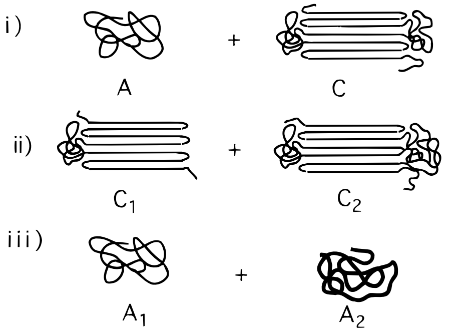

Figure 1. Illustration of the three categories of blends investigated in this study. (i) crystalline and amorphous; (ii) crystalline and crystalline; (iii) amorphous and amorphous.

Additionally, TOF static SIMS measurements on the partially deuterated PEE films were collected on a Charles Evans Associates TFS surface analyzer at Exxon which is equipped with a liquid Ga$^+$ ion source. Spectra were collected in the bunched mode (0.625 ns pulse width) with the ion source operated at 15 keV. Under these conditions, mass resolution was ~3000. Beam current was 600 pA, spot size was 5 mm, area sampled was 64 mm^2, total ion dose/cm^2 for positive and negative spectra was 5.2×10^{12} and 3.0×10^{12}, respectively. Spectrometer vacuum during data collection was 1.3×10^{-7} Pa.

3. Results

Spectra of individual components are discussed in section (a). Several combinations of binary polymer blends were investigated by static SIMS. Spectra of blends are categorized below according to their component crystallinities: (b) crystalline + amorphous, (c) crystalline + crystalline, (d) both amorphous. Figure 1 schematically illustrates these different combinations of polymer blends.

(a) Spectra of Individual Components. Interpretation of the positive and negative SIMS spectra from the individual components and procedures for determining surface purity of each sample are presented in this section. In Figure 2, 2−100 u (u is the SI unit replacing the commonly encountered amu) portions of the positive ion static SIMS spectra recorded for two of the pure polymers, d-LLDPE and EC12, are shown as examples. Selected ion fragment identifications are also provided on the figures. Figure 2 illustrates the dramatic effect on the spectrum due to deuterium labeling and demonstrates that the surface of the sample is not contaminated with foreign hydrogenous material. All the prominent peaks in the positive ion spectrum are shifted from odd masses due to $C_mH_n^+$ fragments (where n is odd) to even masses due to $C_mD_n^+$ (where again n is odd). A similar result is observed in the 2−100 u negative ion spectrum of d-LLDPE as well (Figure 3).

Nearly all the major lines in both the positive and negative ion spectra of d-LLDPE, d-PEP, d-PEE, and d-HDPE appear at even mass units, while those for the amorphous polyethylene EC12 and all other hydrogenous polymers appear at odd mass units. Under these circumstances, which prevail throughout this study, nearly all the major lines for the pure hydrogenous and (per)deuterated polymers are out of registry with one another. Although the stoichiometries of the two polymers in each blend are identical—CH$_2$ (CD$_2$)—differences

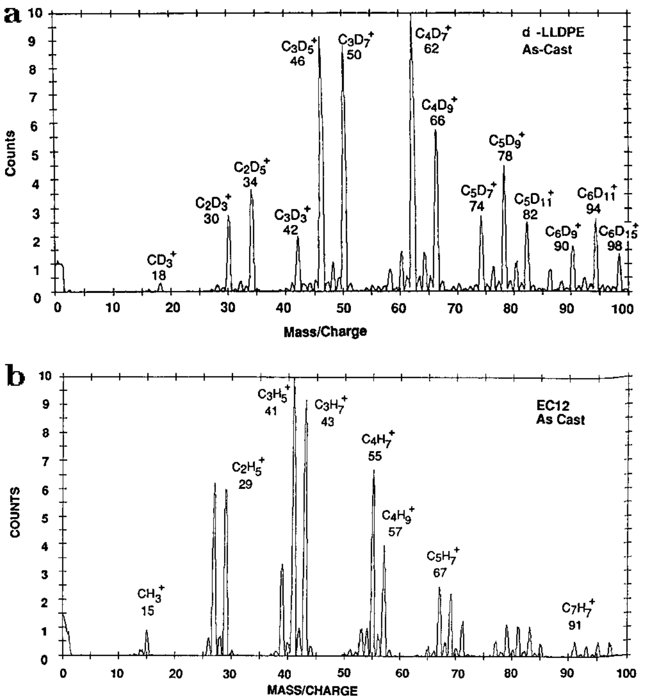

Figure 2. (a) 2–100 u portion of positive ion static SIMS spectrum of perdeuterated-LLDPE, as cast, illustrating the shift of all prominent peaks in the spectrum to even mass units. (b) 2–100 u portion of positive ion static SIMS of EC12, as cast; all major ion fragment peaks are at odd mass units.

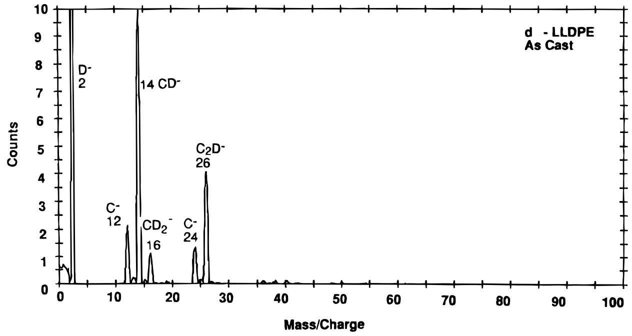

Figure 3. 2–100 u portion of negative ion static SIMS of as-cast pure perdeuterated-LLDPE. Note the absence of peaks of significant intensity at odd mass units, indicating that surface is free from contamination or oxidation.

in polymer architectures and the deuterium labeling of one component in each blend pair ensure that the positive and negative ion SIMS spectra exhibited by one component are easily distinguished from those of the other.

The impact due to deuterium on the ion intensity distribution has been examined in three pairs: d/h-LLDPE, d/h-PEE, and d/h-PEP. The mass-normalized positive ion spectrum residue resulting from subtraction of the d spectrum from the corresponding h spectrum for PE is shown in Figure 4. By normalizing the spectra to account for differences in mass, it is clear that fragmentation patterns for the perdeuterated and hydrocarbon polymers are similar. Nonetheless, the intensity of the positive ion static SIMS of the perdeuterated polymers peaks in the $C_4D_m^+$ manifold, whereas for the hydrogenated polymers, it peaks in the $C_3H_m^+$ manifold. This shift in ion yield intensities is opposite to that resulting from quadrupole instrument sensitivity, which is roughly inversely proportional to mass. The shift in intensity to higher normalized masses for the perdeuterated polymer could be due to differences in C–H and C–D bond dissociation energies. It is known that C–D bond dissociation energies are about 4% larger than C–H bond dissociation energies. This effect was not important for the present study and was hence not investigated further.

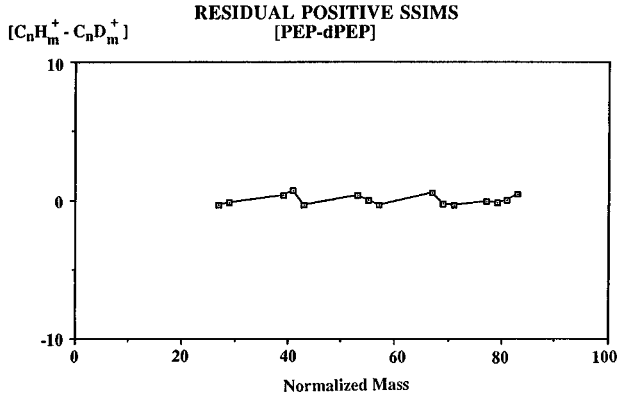

Figure 4. Mass-normalized residual for subtraction of positive static SIMS: PEE–dPEE.

Introduction of oxygen through contaminants or oxidation of the pure polymers and blends could adversely affect the findings of the present study. Consequently, care was taken to ensure that the surfaces were not oxidized or contaminated with oxygenated material. Surface oxidation is manifested by peaks at 16 and 17 u (O^- and OH^-) in the negative ion SIMS. The near absence of signals at 16,17 u for hydrogenous polymers or 16,17,18 u for deuterated polymers [see Figure 3 for example) in these spectra shows that the surfaces are not oxidized to a significant extent. Contamination of a blend or blend component, before or after preparing the blend or blend component thin film, can also adversely impact the positive ion spectra or complicate their interpretation. A common contaminant is siloxane polymer/oligomer—usually poly(dimethylsiloxane). In some cases, siloxane polymer/oligomer contaminant was identified on the surfaces of spin-cast samples based on characteristic peaks in the positive ion spectra—at 28, 73, and 147 u[19a] For the most part, contamination was often not detectable. Data were rejected if the surface O/C stoichiometry exceeded 0.02 (deduced from calibration of SIMS by XPS[8]).

In general, secondary ion yields from two different polymers can vary greatly, and these differences must be taken into account in the process of determining quantitatively the surface composition of a surface which consists, or could consist, of contributions from two different polymers. The distribution of positive and negative secondary ion yields is strongly influenced by the ionization potentials/electron affinities of the fragments and the matrix from which the fragments came ("matrix effects"), as well as by the connectivity of the atoms comprising the molecules studied (for example, geometric isomers).

However, in the present study, matrix effects are sensibly constant. Ionization potentials and electron affinities of all the components are closely matched. Only the connectivities and chain organization (crystalline and amorphous) of the components in each blend are different. This is expected to have only a minor effect on the overall yield of positive and negative ions but can have a marked effect on the fingerprint pattern for the positive ions. To the degree examined, connectivity and degree of crystallinity appear to have no substantial effect on the negative ion yield or its pattern.

Table 2. Ratio of Peak Intensities versus Extent of Deuterium Labeling (Negative SIMS)

polymer	stoichiometric mol % D	intensity ratio $[14^-/(13^- + 14^-)]$	intensity ratio $[26^-/(25^- + 26^-)]$
h-PEP	0	0.116	0.035
h-(1-C_{10})$_x$	0	0.115	0.028
PEE-73	25	0.25	0.27
PEE-90	76	0.635	0.70
d-LLDPE	100	0.97	0.98
d-PEE	100	0.97	0.98

Table 3. Cumulative Carbon Intensities versus Extent of Deuterium Labeling

polymer	stoichiometric mol % D	intensity (+) × 10^3			intensity (−) × 10^3	
		ΣC	ΣC_2	ΣC_3	ΣC	ΣC_2
PEP	0	44	129		709	102
PEE-73	25	38	81	67	783	81
PEE-90	76	45 (43)	111 (96)	70	761 (754)	80 (79)

[a] Values in parentheses indicate data reproducibility.

For polyolefins, negative ion fragmentation patterns are straightforward as higher mass fragments are generally much weaker and therefore of little analytical value. Thus, a straightforward and reliable approach for quantifying the surface composition of a blend comprised of one perdeuterated, saturated polyolefin and one hydrogenated, saturated polyolefin is based on the simple relationship

$$\frac{[CD^- + CD_2^-]}{[CH^- + CH_2^- + CD^- + CD_2^-]} = \text{fractional surface area coverage by deuterated polymer} \quad (1)$$

In each case, CD^- and C_2D^- intensity is derived by correcting for the small contributions from CH_2^- and $C_2H_2^-$ to the 14 and 26 mass peaks, respectively. It is conceivable that substitution of hydrogen with deuterium might change the ion yield so that the intensity ratio given by eq 1 would not accurately reflect the ratio of surface coverage of the polymer components. We have tested this possibility in the following ways. First, we have determined whether the relative yields $[CD^-/CH^-]$ and $[C_2D^-/C_2H^-]$ equal the D/H ratio in each polymer. The [D/H] ratio measured from the negative static SIMS of each polymer is compared with that expected from bulk stoichiometry in Table 2, indicating that there is reasonable agreement between the bulk and SIMS analysis of copolymer stoichiometry (accuracy to within about 10%).

Additionally, a set of experiments was carried out in which the sum of channel intensities of each manifold ($CH_xD_y^+$, $C_2H_xD_y^+$, $C_3H_xD_y^+$) was determined for the positive and negative TOF-SIMS spectra of a series of polyolefins in which the deuterium content ranged from 0 to 75 mol %. The intensities measured are summarized in Table 3. These data show that the intensity does not systematically increase or decrease with deuterium content. In addition, the intensity ratio of the CD^-/CH^- and C_2D^-/C_2H^- peaks is nearly proportional to the D/H ratio present in each polymer (data collected for 0, 26, 75, and 100 mol % D). Taken together, the data in Tables 2 and 3 provide evidence that SIMS intensity ratios, such as are used in eq 1, provide a direct measure of the surface coverage which is consistent with previously reported SIMS data. Accordingly, eq 1 is used to determine the surface composition of each of the blends listed in Table 4.

Table 4. Approximate Surface Compositions[a] of Spin-Cast Films of Blends Consisting of an Amorphous Polymer and a Crystallizable Polymer

amorphous polymer	crystallizable polymer (deuterated component)	approx area % amorphous polymer on Surface[c]
EC12 (0)	d-HDPE (100)	0
EC12 (2)	d-HDPE (98)	~98
EC12 (5)	d-HDPE (95)	~98
EC12 (20)	d-HDPE (80)	~98
EC12	d-HDPE	~100
EC12	d-LLDPE[b]	98
PEP	d-LLDPE	23
d-PEP (20)	NMWD HDPE (80)	100
d-PEP (20)	BMWD HDPE (80)	46

[a] Bulk composition 50:50 by mass unless noted otherwise. [b] 0.918 density "LLDPE" is deuterated 1,4-poly(perdeuteriobutadiene) containing 7% 1,2 defects. [c] Based on ratio of CD^-/CH^-.

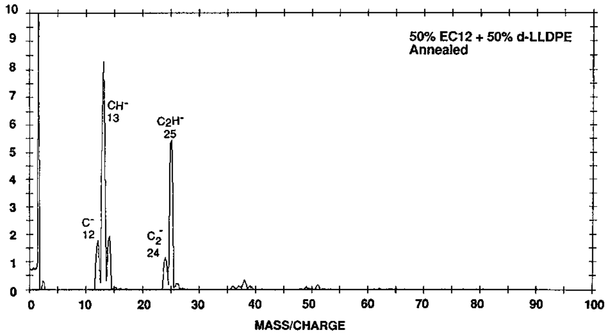

Figure 5. 2−100 u portion of negative ion static SIMS spectrum of annealed blend (50:50 by mass) of EC12 and d-LLDPE.

(b) Crystalline−Amorphous Blends. These blends consisted of a crystalline polymer corresponding to one of the following: high-density polyethylene (HDPE) of narrow (NMWD) or broad (BMWD) molecular weight distribution, medium-density polyethylene (MDPE), or hydrogenated 1,4-polybutadiene, which is often considered a model linear low-density polyethylene (LLDPE). The crystalline component was mixed with an amorphous polymer: poly(ethylethylene) (PEE), poly(ethylenepropylene) (PEP), or poly(ethylene-*co*-dodecene) (EC12). Surface and bulk film compositions (ranging from 2 to 50% amorphous polymer) are tabulated in Table 4. An example of the negative ion spectra recorded is shown in Figure 5. In most instances, the surface composition of a blend is readily seen to be predominantly one component (the amorphous one), as both the positive (not shown) and negative ion mass spectral fragmentation patterns for the blend can be matched with the corresponding spectra of one pure component. For example, the surface of the 20:80 by mass blend of amorphous EC12 with NMWD d-HDPE consists entirely of the EC12 (see Figure 2b). Surface compositions of two other blends of NMWD d-HDPE + amorphous EC12 all exceed 95% of the amorphous component, EC12, even though their average compositions in the film were only 5 and 2 mass %. Annealing these blends did not change the surface compositions. The surface enrichment of EC12 in these thin-film compositions is illustrated in Figure 6, along with other binary combinations of EC12 with semicrystalline and amorphous polymers for comparison. From the surface composition obtained from a blend of EC12 + d-LLDPE, we find that the above observations can hold even for a blend where the crystalline polymer (d-LLDPE) has a much lower degree of crystallinity (ca. 40%). In this case, the fraction of semicrystalline polymer at the

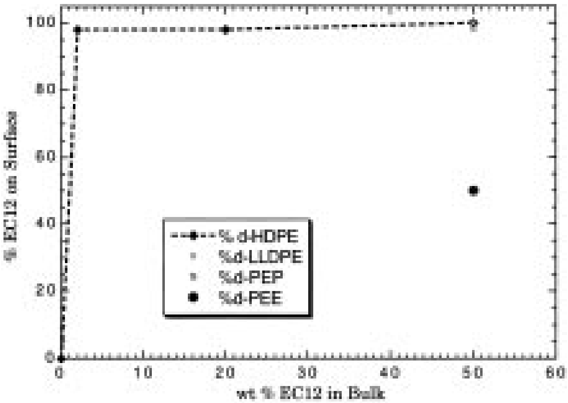

Figure 6. Surface composition versus bulk composition for a series of binary blends of EC12. All surface compositions were determined from negative static SIMS.

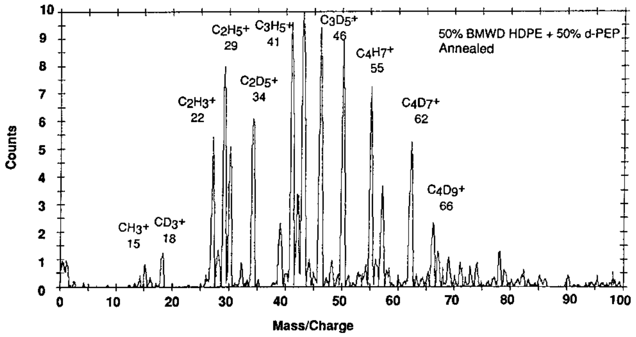

Figure 7. 2−100 u portion of positive ion static SIMS of blend (50:50 by mass) of d-PEP and BMWD HDPE.

surface is significantly higher (≈40−45%). Presumably, the amorphous regions of the semicrystalline polymer, d-LLDPE, compete with the amorphous copolymer, EC12, for surface enrichment in this case. In most of the cases studied, however, the amorphous polymer dominates the surface composition (>95%) even when it is present at low concentrations in the bulk.

The polydispersity of the polymers provides another parameter which can be used to control surface segregation, particularly in the case where the crystalline component is polydisperse and the amorphous component has a high surface tension. The competitive influence of polydispersity, crystallinity, and surface tension of the polymers can be used to fine tune the surface composition. As an illustration of this effect, we consider a blend of a relatively higher surface tension amorphous polymer (see section d), d-PEP, with a polydisperse crystalline polymer, BMWD HDPE. The 2−100 u portion of the positive ion spectrum for this blend is shown in Figure 7. The spectrum clearly consists of peaks from both crystalline and amorphous components. Based on eq 1, the surface composition is determined to be 50% BMWD HDPE and 50% d-PEP. The MWD of the commercial BMWD HDPE used in this blend is characterized by a very large polydispersity index (35), and this polymer thus contains a substantial amount of low molecular weight polymer. Polymer bulk crystallinity is on the order of 70% even after annealing the sample. It seems probable in this case that a small portion of the low molecular weight fraction of this HDPE is amorphous at room temperature, giving rise to a competition for the surface with the amorphous d-PEP.

Table 5. Approximate Surface Compositions[a] of Spin-Cast Films of Blends Consisting of Two Crystallizable Polyethylenes

lower density polyethylene[b]	higher density polyethylene[c]	approx area % lower density polyethylene on surface
d_8-LLDPE	NMWD HDPE	98
d_8-LLDPE	BMWD HDPE	20
d_8-LLDPE	MDPE	18

[a] Bulk composition 50:50 by mass. [b] The 0.918 density LLDPE is deuterated 1,4 (perdeutero)polybutadiene. [c] All entries in this column are hydrogenous.

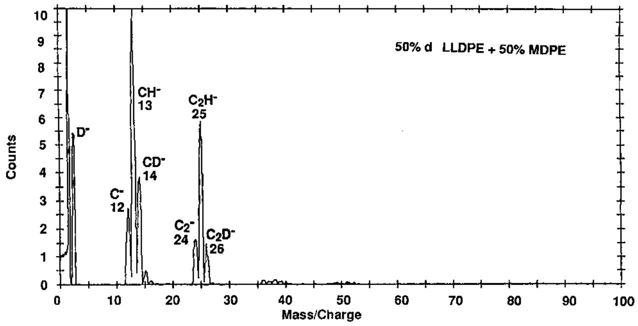

Figure 8. 2−100 u portion of negative ion static SIMS of as-cast blend (50:50 by mass) of d-LLDPE and MDPE.

(c) Blends of Two Crystallizable Polyolefins. Surface compositions of blends of semicrystalline polymers were also studied (see Table 5). These films contained two crystalline components wherein the crystallinity of one component was markedly different from the other. The positive and negative ion spectra of d-LLDPE + NMWD HDPE are almost identical to the spectra of pure d-LLDPE (Figures 2 and 3), illustrating that the surface is completely covered by the polymer having the lower crystallinity (d-LLDPE). However, as expected from polydispersity effects, a blend of d-LLDPE and BMWD HDPE (MWD ∼ 35) showed a lower surface coverage of d-LLDPE (∼20%). Figure 8 shows the negative static SIMS ion spectra of yet another blend film where the component crystallinities are closely matched, d-LLDPE with MDPE (MWD ∼ 2) (50 wt %; annealed). For this sample, the surface is comprised of ∼18% d-LLDPE and ∼82% MDPE. Such a lower percentage of d-LLDPE on the surface compared to MDPE may be due to two factors: the poor match in molecular weight between these two polymers [the MDPE has a substantially lower molecular weight compared to d-LLDPE (M_n ≈ 30K vs 108K)], and the broader MWD of the MDPE (2) versus the d-LLDPE (1.1). The positive (0−200) and negative spectra (0−100) of d-LLDPE blended with either BMWD HDPE or MDPE are quite similar, indicating that the surface behavior of the BMWD HDPE is similar to that of MDPE of a lower molecular weight. This suggests that the lower molecular weight fraction in the polydisperse HDPE sample is preferentially enriched at the surface, and this finding is consistent with the findings of section (b).

(d) Blends of Two Amorphous Polyolefins. The blends examined were binary combinations of the three amorphous polymers—dPEP, d-PEE, and EC12 (see Table 6). Before we examine the spectra of blends of these three amorphous polyolefins, an illustration of the extent of enrichment at a surface which results only from differences in surface tension (γ) is provided by the following experiment. A blend containing only 2 mass % (polymethylsiloxane) (PDMS) and 98% EC12 was prepared and cast as a thin film from toluene. This blend was annealed at 140 °C in vacuo. The positive and negative static SIMS spectra recorded for the blend

Table 6. Surface Compositions of Spin-Cast Films of Blends[a] Consisting of Two Amorphous Polyolefins

hydrogenous amorphous component A	perdeuterated amorphous component	approx area % hydrogenous component on surface
EC12	d-PEE	50
EC12	d-PEP	100
PEP	d-PEE	0

[a] All blends 50:50 by mass.

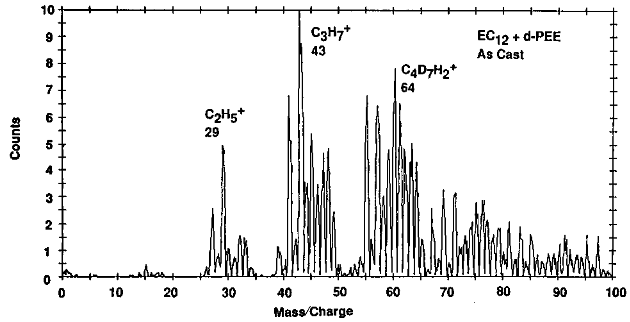

Figure 9. 2−100 u portion of positive ion static SIMS of as-cast blend (50:50 by mass) of EC12 and d-PEE.

were indistinguishable from those recorded for the pure PDMS.[19] These results can be explained on the basis of the difference of surface tension between the two polymers. The surface tension of amorphous hydrocarbon polymers is typically found to be in the range of (28−34) × 10^{-3} N/m,[20−27] whereas the surface tension of PDMS is (19.5−21) × 10^{-3} N/m.[28,29] As expected, there is a strong tendency for the lower surface tension polymer to segregate to the air surface.

Positive and negative ion static SIMS of equal mass percent blends of amorphous polyolefins EC12 + d-PEE show that the surface is only slightly enriched in d-PEE (~56%), suggesting similar surface tension for the two polymers. In contrast, a mixture of PEP and d-PEE showed almost 100% d-PEE on the surface. Likewise, the spectra of a blend of 50% dPEP + 50% EC12 showed the surface to be comprised of over 90% EC12. As with the blend of d-PEE + d-PEP,[12] the substantial enrichment of EC12 at this surface is attributed to the smaller value of the “segmental asymmetry parameter” β[11,12] and/or to the lower dispersive surface tension of EC12.

The blend (EC12 + d-PEE) gave a unique positive static SIMS which is not simply the weighted average sum of the spectra for the two components, but also contains several lines which are not present in the spectrum of either component. These new lines likely result from the dynamics of the fragmentation process in which H and D are exchanged between the two hydro (deuterio) carbon chains.[30] It is inferred from this result that the two polyolefin chains are substantially compatible, or miscible, at the surface. This aspect is beyond the scope of the present paper.

4. Discussion

In 1962, Flory proposed that the crystalline regions in semicrystalline homopolymers exclude the amorphous regions and that a well-defined crystal−amorphous “interface zone” exists which separates the crystalline and amorphous regions. It is expected on the basis of this argument that an enrichment of the amorphous interface of semicrystalline polymer occurs at the free surface of thin films. Likewise, in a mixture of an amorphous homopolymer (or copolymer) and a semicrystalline polymer, the amorphous polymer can be expected to segregate to the surface. This kind of segregation is also suggested by observations of segregation of the flexible component of block copolymers and blends to a free boundary in recent measurements.[10−13] In the present study, the degree of surface segregation is studied as a function of polymer crystallinity. By blending amorphous and semicrystalline and comparing these blends to two semicrystalline polymers, we distinguish between surface enrichment of externally added amorphous homopolymer and the enrichment of amorphous regions of the crystalline polymer present at the transition region of the chain fold boundaries.

The surface compositions of model polyolefin blends are determined based on the assumption that the fragmentation pattern and ion yield of each blend component is an invariant with the surface composition because of the close match in component ionization potentials, electron affinities, and compositions. This hypothesis is verified using randomly deuterated amorphous copolymers. For blends, in most instances the surface composition is dominated by one component, as the mass spectral fragmentation pattern for the blend can be largely or wholly matched with the spectrum of one pure component. For consistency, the surface composition of each blend is determined from the ratio of intensities of the CH^- and CD^- peaks in the negative ion spectra. Thus, the ratio of $[CD^- + CD_2^-]/[CH^- + CH_2^-]$ ion yields provides an estimate of the fraction of surface covered by the deuterated polymer.

It is found for a series of amorphous and semicrystalline hydrocarbon polymers of approximately matched molecular weights that the amorphous component predominantly occupies the surface. As opposed to previous studies,[15,16] static SIMS is employed to *quantitatively* estimate the degree of surface segregation rather than as a qualitative probe into surface segregation. A greater fraction of the surface is given over to the component having less crystallinity. For the blends of amorphous hydrocarbon polymers PEE and EC12 on the other hand, the surface is cohabited by the two components in direct proportion to their concentration in the bulk. This is not the case for either PEE or EC12 blended with d-PEP. In these cases, the surface is covered by PEE or EC12. These findings are consistent with earlier results that are explained on the basis of differences in chain flexibility.[10−13] We add that enthalpic factors may also play a role in determining the overall surface free energy, and the surface wetting species and the degree of crystallinity should only predominate when these other factors are relatively small.

The surface compositions of three blends of HDPE + amorphous polyolefin all exceed 95% amorphous polyolefin even though the bulk composition of amorphous polyolefin is only 2−50 mass %. Previous experimental studies have shown that, in the absence of other dominating effects, surfaces of blends of matched hydrogenated and perdeuterated polymers are composed of virtually 100% perdeuterated polymer due to isotopic enthalpic differences. In the blends examined in this study, the isotopic roles of the crystallizable and amorphous polymers used have been exchanged; in some cases the crystalline polymer was deuterated and in others the amorphous polymer was deuterated. The surface behavior of blends of crystalline and amorphous polymers was not affected by the reversal of isotopic labeling, however. We conclude that the degree of crystallinity is an important or dominant factor governing surface segregation.

Acknowledgment. We are indebted to Dr. Mohan Sikka and Prof. Riccardo Levi-Setti for useful discussions. We also thank the Center for Interfacial Engineering at the University of Minnesota for a grant to carry out this research, Exxon Chemical Co. for release of this information, and Dr. Sushil Satija (NIST) for the film thickness measurements by neutron reflectivity. We thank Dr. Bill Katz and Dr. Gary Smith at Evans Central, Minnesota, for assistance with SIMS.

References and Notes

(1) (a) Boyd, R. H. *Polymer* **1985**, *26*, 323. (b) Hill, M. J.; Barham, P. G.; Keller, A. *Polymer* **1992**, *33*, 2530−2541. (c) Mandelkern, L.; Peacock, A. J. Proceedings of an International Course and Conference on the Interfaces between Mathematics, Chemistry, and Computer Science *Studies in Physical and Theoretical Chemistry* **1987**, *54*, 201−227. (d) Peacock, A.; Mandelkern, L. *J. Polym. Sci., B* **1990**, *28*, 1917. (e) Popli, R.; Mandelkern, L. *Polym. Bull.* **1983**, *9*, 260. (f) Voigt-Martin, D. G.; Alamo, R.; Mandelkern, L. *J. Polym. Sci., Polym. Phys. Ed.* **1986**, *24*, 1283. (g) Alamo, R.; Domszky, R.; Mandelkern, L. *J. Phys. Chem.* **1984**, *88*, 6547. (h) Randall, J. C. *J. Polym. Sci., Polym. Phys. Ed.* **1973**, *11*, 275. (i) Perez, E.; Vanderhart, D. L. *J. Polym. Sci., Polym. Phys. Ed.* **1987**, *25*, 1637. (j) Runt, J. P.; Brown, C. A.; Zhang, X. F.; Kumar, S. K. *Macromolecules* **1991**, *24*, 3466.

(2) Thomas, H. R.; O'Malley, J. J. *Macromolecules* **1981**, *14*, 1316.

(3) Anastasiadis, S. H.; Chen, J. K.; Koberstein, J. T. *Polym. Eng. Sci.* **1986**, *26*, 1410.

(4) Dwight, D. W.; McGrath, J. E.; Riffle, J. S.; Smith, S. D.; York, G. A. *J. Electron Spectrosc. Relat. Phenomena* **1990**, *52*, 457.

(5) Ratner, B. D.; Weathersby, P. K.; Hoffman, A. S.; Kelly, M. A.; Sharpen, L. H. *J. Appl. Polym. Sci.* **1978**, *22*, 643.

(6) Thompson, P. *Anal. Chem.* **1991**, *63*, 2447.

(7) Clark, D. T.; Peeling, J.; O'Malley, J. J. *J. Polym. Sci., Polym. Chem. Ed.* **1976**, *14*, 543.

(8) (a) Parsonage, E.; Tirrell, M.; Watanabe, H.; Nuzzo, R. *Macromolecules* **1991**, *24*, 1987. (b) Calibration plots have been constructed previously for the relationship between the $[(O^- + OH^-)/(C^- + CH^- + CH2\text{-})]_{SIMS}$ and $[O/C]_{XPS}$ stoichiometric ratio (20° take-off angle) for corona discharge treated polyethylenes and polypropylenes (see, for example: Gardella, J. A., Jr.; Hercules, D. M. *Anal. Chem.* **1980**, *52*, 226). From these calibrations, it is clear that static SIMS is at least as sensitive to adventitious surface oxidation/impurities as XPS. A criterion was adopted that the $[(O^- + OH^-)/(C^- + CH^- + CH_2^-)]_{SIMS}$ ratio must be lower than a limiting value (corresponding to a surface $[O/C]_{XPS}$ of $\sim$0.02 or less) before the data for a given thin film were used.

(9) (a) Bates,F. S.; Fetters, L. J.; Wignall, G. D. *Macromolecules* **1988**, *21*, 1086. (b) Jones, R. A. L.; Norton, L. J.; Kramer, E. J.; Composto, R. J., Stein, R. S.; Russell, T. P. Mansour, A.; Karim, A.; Felcher, G. P.; Rafailovich, M. H.; Sokolov, J.; Zhao, Z.; Schwarz, S. A. *Europhys. Lett.* **1990**, *12*, 41.

(10) (a) Sikka, M.; Singh, N.; Karim, A.; Bates, F. S.; Majkrzak, C. F.; Satija, S. K. *Phys. Rev. Lett.* **1993**, *70*, 207. (b) It should be realized that compressibility effects are important in polymer blends and that the separation of the interaction parameters into "entropic" and "enthalpic" contributions is somewhat artificial.

(11) Fredrickson, G.; Donley, J. P. *J. Chem. Phys.* **1992**, *97*, 8941.

(12) Sikka, M.; Singh, N.; Bates, F. S.; Karim, A.; Satija, S.; Majkrzak, C. F. Surface Segregation in Model Symmetric Polyolefin Diblock Copolymer Melts. *J. Phys II (Fr)* **1994** *4*, 2231.

(13) (a) Steiner, U.; Klein, J.; Eiser, E.; Budkowski, A.; Fetters, L. J. *Science* **1992**, *258*, 1126. (b) Jones, R. A. L.; et al. *Phys. Rev. Lett.* **1991**, *66*, 1326; *Europhys. Lett.* **1990**, *12*, 41.

(14) Hearn, M. J.; Briggs, D. Yoon, S. C.; Ratner, B. D. *Surf. Interface Anal.* **1987**, *10*, 384. The above reference relates to the penetration depth of static SIMS. Under these conditions, typical penetration depths expected for these systems is between 10 and 30 Å.

(15) Brinkhuis, R. H. G.; Van Ooij, W. J. *Surf. Interface Anal.* **1988**, *11*, 214.

(16) (a) Kramer, E.; Hearn, M. J.; Briggs, D. *Surf. Interface Anal.* **1988**, *11*, 198. (b) Newman, J. G.; Viswanathan, K. V. *J. Vac. Sci. Technol. A* **1990**, *8* (3), 2388.

(17) Certain commercial equipment, instruments, and materials are identified in this article in order to adequately specify experimental procedure. Such identification does not imply recommendation or endorsement by NIST, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

(18) (a) Benninghoven, A. *Surf. Sci.* **1975**, *53*, 596. (b) Benninghoven, A. *J. Vac. Sci. Technol. A*, **1985**, *3*, 451.

(19) (a) Briggs, D.; Brown, A.; Vickerman, J. C. *Handbook of Static Secondary Ion Mass Spectrometry*; John Wiley & Sons: New York, 1990. (b) Affrossman, S.; Hartshorne, M.; Jerome, R.; Munro, H.; Pethrick, R. A.; Petitjean, S.; Rei Vilar, M. *Macromolecules* **1993**, *26*, 5400.

(20) Hildebrand, J. H.; Scott, R. L. *The Solubility of Non-Electrolytes*, 3rd ed.; Reinhold: New York, 1959.

(21) Hansen, C. M. *J. Paint Technol.* **1967**, *39*, 104.

(22) Schonhorn,H.; Ryan, F. W. *J. Phys. Chem.* **1966**, *70*, 3811.

(23) Schonhorn, H. *Macromolecules* **1968**, *1*, 145.

(24) Wu, S. *J. Polym. Sci., Part C* **1971**, *34*, 19.

(25) Roe, R. J. *J. Phys. Chem.* **1968**, *72*, 1013.

(26) Dutton, R. H.; Johnson, R. E., Jr. *J. Colloid Interface Sci.* **1966**, *21*, 367.

(27) Cormia, R. L.; Price, F. P.; Turnbull, D. *J. Chem. Phys.* **1962**, *37*, 1333.

(28) Greenhill, E. B.; McDonals, S. R. *Nature* **1953**, *171*, 37.

(29) Dee, G. T.; Sauer, B. B. *Macromolecules* **1993**, *26*, 2771.

(30) Chilkoti, A.; Castner, D. G.; Ratner, B. D. *Appl. Spectrosc.* **1991**, *45*, 209.

MA951349N