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Surface enrichment-depletion duality in a binary polymer blend

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Abstract. – We have measured the surface segregation towards the vacuum in films of a binary mixture of deuterated $E_{48}EE_{52}$ (d52) —and hydrogenous $E_{38}EE_{62}$ (h66)— random olefinic copolymers. Here E and EE are the linear ethylene and branched ethyl ethylene groups (C_4H_8) and [$C_2H_3(C_2H_5)$], respectively. The d52 copolymer is enriched at the surface when d52 is the minority component in the blend. On the contrary, the surface is depleted in the d52 chains, when they constitute a majority of the mixture. We have determined two branches of the segregation isotherm corresponding to the enrichment and the depletion. A mean-field Cahn model describes consistently these two isotherm branches. The observed enrichment-depletion duality modifies a common viewpoint on surface segregation.

The free surface of a binary mixture of partially miscible polymers (A and B) may favor one of the components, leading to a blend composition at the surface different from that in the bulk [1-4]. Commonly the surface composition decays smoothly to its bulk value within a finite microscopic characteristic length [5, 6]. Also macroscopically thick wetting layers were observed [7, 8], where the second coexisting phase intrudes between the vacuum surface and the saturated bulk phase. The surface concentration and phase morphology determine interfacial properties such as adhesion, frictional properties or wear resistance. Apart from the practical implications, there are important not completely resolved basic questions concerning surface enrichment or wetting phenomena [9, 10]. These include the issue of the partial- to complete-wetting transition, the order of this transition, and indeed an understanding of the factors that drive either one or the other polymer to the surface.

According to a common viewpoint [11] the free surface is enriched: i) in the component A with lower cohesive energy, ii) regardless of the value of the bulk composition ϕ_∞. This

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opinion has been recently modified: i) Entropic effects driving the segregation of the higher-energy B polymers were predicted [12] and demonstrated experimentally [13-15]. ii) An enrichment-depletion duality was advocated by mean-field (MF) analysis [16-18] and observed in Monte Carlo simulations [18,19]: It is expected that some mixtures could exhibit the surface enrichment in the component A, when a bulk composition ϕ_∞ is below a certain value Q, and the depletion in A for $\phi_\infty > Q$.

The duality phenomenon plays an important role in the reduction of the miscibility gap expected for polymer blends confined in thin films between symmetric walls [18, 19]. It is also a prerequisite [17] for the critical (2nd order) wetting transition, observed so far only for small-molecule mixtures [20] but not for polymer blends [21].

In this letter we describe the first experimental study of the surface enrichment-depletion duality observed for a polymer mixture. The change of the blend component segregating to the free surface is examined at temperatures close to an upper critical temperature T_c.

The mixture under investigation is composed of random poly(ethylene(E)-ethyl ethylene (EE)) copolymers $\mathrm{E}_{1-x}\mathrm{EE}_x$ of mean microstructure $(\mathrm{C_4H_8})_{1-x}(\mathrm{C_2H_3(C_2H_5)})_x$. Such blends, where two components have different EE fractions x_1 and x_2, create an attractive model system, as bulk and surface interactions may be tailored by a suitable choice of x values [15, 22-24]. The pair used in this study consists of copolymers h66 and d52 with x equal to 66% and 52%, respectively. The d52 copolymer is partly deuterated with 34% of hydrogen replaced by deuterium. The weight-averaged degrees of polymerization are $N_{\mathrm{d52}} = 1510$ and $N_{\mathrm{h66}} = 2030$ (the polydispersity index < 1.08 for both polymers). The statistical segment lengths $a_{\mathrm{d52}} = 0.716$ nm and $a_{\mathrm{h66}} = 0.669$ nm are taken from ref. [25]. The coexistence curve of the d52/h66 mixture (with $T_\mathrm{c} = 88(4)$ °C) was determined previously [22, 25]. The binodal is described [22] within the Flory-Huggins model with an interaction parameter $\chi = (0.466/T - 1.237 \cdot 10^{-4})\ (1 - 0.03\ \phi)$, dependent on the d52 concentration ϕ. Neither blend component segregates to the interface with a substrate [23]. Films of about 350–700 nm thickness with various overall d52 concentration were spin-cast on gold-covered silicon wafers and annealed in high-stability ($\Delta T = 1$ °C) vacuum ($< 10^{-3}$ Torr) ovens at temperatures of 71 and 92 °C. Then they were quenched and stored at temperature below the glass transition (< -63 °C) until their composition profiles could be analyzed. The concentration ϕ *vs.* depth z profiles $\phi(z)$ of the deuterated d52 component within the samples (normal to the free surface) were measured using nuclear-reaction analysis (NRA). In this method (described in detail elsewhere [26,27]) ^{3}He particles are incident on the polymer film, and as they penetrate it the reaction $^2\mathrm{H}(^3\mathrm{He}, {}^1\mathrm{H})^4\mathrm{He}$ with the ^{2}H labels takes place at different depths. The composition profiles $\phi(z)$ are obtained from the energy spectra of the forward-emitted α-particles (^{4}He) [26] or the protons (^{1}H) detected in the backward direction [27]. The proton detection mode enables the position of the zero depth ($z = 0$, fig. 1b)) to be determined with a reproducibility better than 1 nm [23]. All studied samples were examined by an interference microscopy, which showed their lateral homogeneity.

Figure 1 presents typical equilibrium profiles for the d52 copolymer constituting the minority (fig. 1a)) and majority (fig 1b), c)) of the blend. While an *enrichment* at the free surface is directly seen in the first situation (traced with the α-particles), a *depletion* in the second case could be deduced thanks to a reference deuterated layer, pointing the exact surface ($z = 0$ nm) position. Such a reference layer was measured prior to the annealed sample (in the p-detection mode, see fig. 1b)), or simultaneously with it as its top cover (when α-particles were detected, see fig. 1c)). As NRA has a limited depth resolution, an essential observable is the surface excess z^* of the d52 component:

$$z^* = \int_0^{z(\phi_\infty)} [\phi(z) - \phi_\infty]\mathrm{d}z\,. \tag{1}$$

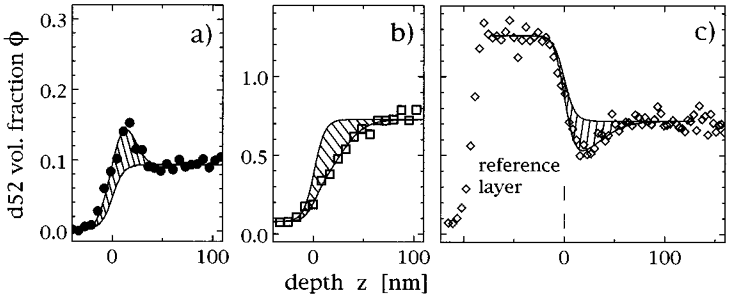

Fig. 1. – Typical composition-depth profiles $\phi(z)$ of the surface region indicating: an enrichment (a)) and a depletion (b), c)) in the d52 component, obtained for 10% d52/90% h66 and 70% d52/30% h66 monolayers annealed at 71 °C for 16 and 43 hours, respectively. Hatched areas mark the positive (a)) and negative (b), c)) surface excess z^* values. The surface ($z = 0$) position, necessary for the z^* evaluation, was yielded by: i) the profile itself [26] (a)); ii) a profile of the control layer measured prior to the annealed sample [23] (b)); iii) an interface created by the reference layer positioned on top of the annealed sample (c)). b) is possible only with the proton detection mode of NRA [23].

Here $z(\phi_\infty)$ is the distance from the surface to the plateau in concentration with the bulk composition ϕ_∞. The *positive* (fig. 1a)) and *negative* (fig. 1b), c)) z^* values are indicated by the shaded areas in figs. 1. Both signs of the surface excess were determined for the bulk concentrations ϕ_∞ denoted by solid and open circles in the phase diagram presented in fig. 2. Systematic studies performed at $T = 71$ °C show the surface enrichment/depletion determined for the bulk compositions ϕ_∞ lower/higher than those of the miscibility gap. The corresponding z^* *vs.* ϕ_∞ relation is shown in fig. 3, with two branches describing the enrichment and the depletion, respectively. These data seem to correspond to a thermodynamic equilibrium: Even 8 times shorter annealing periods resulted in comparable z^* values. This is due to the high mobility [28] of the olefinic copolymers. The weak surface enrichment in d52 determined for low ϕ_∞ values in the one-phase region was confirmed by similar observations made for surface-directed phase separation detected in the samples with average composition $\langle\phi\rangle = 0.4$.

We analyze the segregation data within the Cahn MF description [1-4, 17]. The original treatments [1, 2, 17] of this approach allowed already for the profiles $\phi(z)$ with both positive and negative gradients $\mathrm{d}\phi/\mathrm{d}z$, but did not consider all consequences relevant here. The excess free energy F per unit area of the binary mixture in contact with a planar surface (at $z = 0$) is written as [1-4, 17]

$$F/k_\mathrm{B}T = f_\mathrm{s}(\phi_\mathrm{s}) + \int_0^\infty [\Delta f + \kappa(\mathrm{d}\phi/\mathrm{d}z)^2]\mathrm{d}z\,. \tag{2}$$

Here a “bare” surface free-energy term f_s depends only on the surface concentration ϕ_s and the integral represents the contribution due to the profile $\phi(z)$. The free energy Δf, needed to create a unit volume of the blend with composition ϕ from a bulk reservoir at composition ϕ_∞, is given by $\Delta f(\phi) = f(\phi) - f(\phi_\infty) - (\phi - \phi_\infty)(\partial f/\partial\phi)_{\phi_\infty}$. Here $f(\phi)$ is the free energy of mixing: $f = \phi \ln\phi/N_\mathrm{d52} + (1-\phi)\ln(1-\phi)/N_\mathrm{h66} + \chi\phi(1-\phi)$, and the gradient energy parameter [4] $\kappa = [(1-\phi)a^2_\mathrm{d52} + \phi a^2_\mathrm{h66}]/[36\phi(1-\phi)]$.

The equilibrium profile $\phi(z)$ must satisfy the differential equation [1-4, 17]

$$\mathrm{d}\phi/\mathrm{d}z = \mp\sqrt{\Delta f/\kappa} \tag{3a}$$

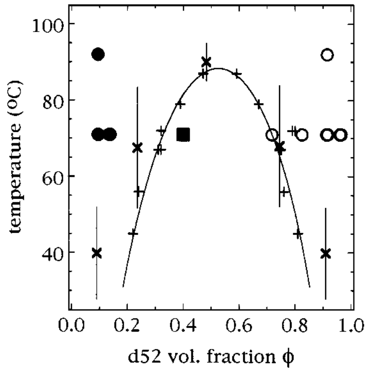

Fig. 2

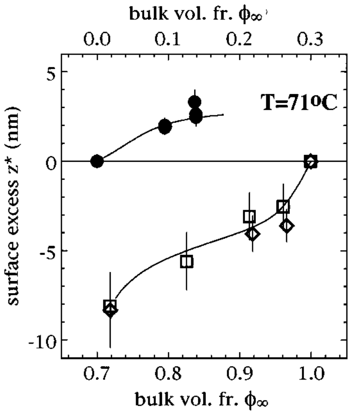

Fig. 3

Fig. 2. – Phase diagram with coexistence compositions (+) and temperatures (×), determined by refs. [22] and [25], independently. The solid line is the binodal calculated [22] for the parameter $\chi = (0.466/T - 1.237 \cdot 10^{-4})(1 - 0.03\phi)$. Bulk $\phi = \phi_\infty$ (•, ○) and average $\phi = \langle\phi\rangle$ (■) compositions in the one- and two-phase region are marked, where the surface enrichment (•, ■) or depletion (○) was concluded.

Fig. 3. – Two branches of the segregation isotherm $z^*(\phi_\infty)$ corresponding to $T = 71$ °C: The positive and negative surface excess z^* values were determined as shown in figs. 1a) (•), b) (□), c) (◇). Two additional points correspond to pure components. The solid lines are calculated from MF model assuming the $(-\mathrm{d}f_\mathrm{s}/\mathrm{d}\phi)_\mathrm{s}$ function presented in fig. 4 as the solid curve.

along with the surface boundary condition

$$-\,\mathrm{d}f_\mathrm{s}/\mathrm{d}\phi(\phi_\mathrm{s}) = -2\kappa(\mathrm{d}\phi/\mathrm{d}z)_\mathrm{s} = \pm 2\sqrt{\kappa(\phi_\mathrm{s})\Delta f(\phi_\mathrm{s})}\,. \tag{3b}$$

Whenever the symbols "±" and "∓" are used, then their upper sign corresponds to the surface enrichment ($\mathrm{d}\phi/\mathrm{d}z < 0$) while the lower one to the depletion ($\mathrm{d}\phi/\mathrm{d}z > 0$). The formula for the surface excess $z^*(\phi_\infty)$

$$z^* = \pm \int_{\phi_\infty}^{\phi_\mathrm{s}} (\phi - \phi_\infty)\sqrt{\kappa/\Delta f}\,\mathrm{d}\phi \tag{4}$$

relates the surface concentration ϕ_s with the experimental observable $z^*(\phi_\infty)$. In turn the excess free energy F_e for the equilibrium profile is given by

$$F_\mathrm{e}/k_\mathrm{B}T = f_\mathrm{s}(\phi_\infty) - \int_{\phi_\infty}^{\phi_\mathrm{s}} [(-\mathrm{d}f_\mathrm{s}/\mathrm{d}\phi) \mp 2\sqrt{\kappa\Delta f}]\mathrm{d}\phi\,. \tag{5}$$

The changes in F_e due to the surface composition ϕ_s variation can be depicted graphically as the Cahn construction [1, 3, 17] (see fig. 4). It presents two quantities $(-\mathrm{d}f_\mathrm{s}/\mathrm{d}\phi)_\mathrm{s}$ (a solid curve) and $\pm 2(\kappa\Delta f)^{1/2}$ (dashed lines calculated for each ϕ_∞) plotted as a function of ϕ_s. The intersections of these two types of relations correspond to the boundary condition of eq. (3*b*).

The procedure outlined in eqs. (4) and (3*b*) yielded for each segregation isotherm point $z^*(\phi_\infty)$ one $(-\mathrm{d}f_\mathrm{s}/\mathrm{d}\phi)_\mathrm{s}$ locus in the Cahn construction of fig. 4. The loci, marked as (•) and (○), correspond to the enrichment —and depletion— data, respectively. They determine a single function $(-\mathrm{d}f_\mathrm{s}/\mathrm{d}\phi)_\mathrm{s}$, shown as a solid curve in fig. 4, which goes to zero at the surface concentration $Q = 0.44$. The $(-\mathrm{d}f_\mathrm{s}/\mathrm{d}\phi)_\mathrm{s}$ function describes well both modes of the surface

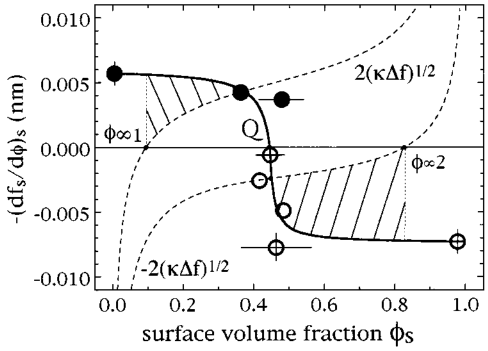

Fig. 4. – Loci describing the concentration ϕ_s dependence of the "bare" surface energy derivative $(-\mathrm{d}f_\mathrm{s}/\mathrm{d}\phi)_\mathrm{s}$ determined for the enrichment ($\bullet$, $z^* > 0$) and depletion ($\circ$, $z^* < 0$) data of fig. 3. The fitted $(-\mathrm{d}f_\mathrm{s}/\mathrm{d}\phi)_\mathrm{s}$ function, marked as a solid curve, changes its sign at Q. Dashed lines indicate for each ϕ_∞ value the corresponding $\pm 2(\kappa\Delta f)^{1/2}$ relations [29]. The boundary condition of eq. (3*b*) is clearly met for the enrichment ($\phi_{\infty 1} < Q$) and the depletion ($\phi_{\infty 2} > Q$) as described in the text.

segregation: for the bulk concentration $\phi_{\infty 1} < Q$ it intersects the corresponding $\pm 2(\kappa\Delta f)^{1/2}$ relation at the *enriched* surface concentration $\phi_\mathrm{s} > \phi_{\infty 1}$, whereas for $\phi_{\infty 2} > Q$ the surface *depletion* ($\phi_\mathrm{s} < \phi_{\infty 2}$) is concluded. The surface segregation is in both cases accompanied by the reduction in the excess free energy F_e indicated by the hatched regions in fig. 4. Finally, using the (single) $(-\mathrm{d}f_\mathrm{s}/\mathrm{d}\phi)_\mathrm{s}$ relation we back-calculated both branches of the segregation isotherm, presented as two solid lines in fig. 3 consistent with the data.

The observed duality phenomenon is related [17,18] with the $(-\mathrm{d}f_\mathrm{s}/\mathrm{d}\phi)_\mathrm{s}$ function changing its sign at surface concentration $0 < Q < 1$, while the standard situation with the surface enriched always in the same component corresponds to $Q < 0$ or $Q > 1$ [1,3,17]. Some of the earlier segregation studies [23,24,30,31], performed for a limited concentration range, exhibit the Cahn constructions with $(-\mathrm{d}f_\mathrm{s}/\mathrm{d}\phi)_\mathrm{s}$ going to zero at $0 < Q < 1$ suggesting experiments verifying the possible duality effect. The non-linear shape of the determined $(-\mathrm{d}f_\mathrm{s}/\mathrm{d}\phi)_\mathrm{s}$ function is similar to that observed for other polyolefine mixtures [15,23,24] and examined in our previous work [23]. The Cahn construction of fig. 4 would predict the critical wetting transition to occur at $T_\mathrm{w} = 86$ °C if the $(-\mathrm{d}f_\mathrm{s}/\mathrm{d}\phi)_\mathrm{s}$ relation was independent of temperature [24]. Still T_w is expected to be located close to the critical point T_c. The enrichment-depletion duality reflects a very small surface energy difference between pure blend components d52 and h66. This is due to the destructive superposition of enthalpic and entropic forces driving the segregation, as described elsewhere [15].

In summary, for a partly miscible binary polymer blend we have observed the free surface always enriched in the minority component for both ranges of the bulk concentration ϕ_∞ close to 0 and to 1. Our results are in accord with expectations based on MF Cahn theory.

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