

INTERFACIAL PHENOMENA IN THIN POLYMER FILMS STUDIED BY DIRECT PROFILING TECHNIQUES

ŠTUDIJ POJAVOV NA MEJNIH PLOSKVAH TANKIH POLIMERNIH PLASTI Z DIREKTNIMI TEHNIKAMI PROFILIRANJA

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Various interfacial phenomena, such as: phase coexistence, surface segregation and wetting, as well as surface directed phase separation, determine many properties of polymer mixtures. These phenomena are studied in blends confined in a thin film geometry. Direct composition vs. depth profiling techniques are used, which have been developed in the last decade. Present paper describes briefly direct profiling methods and interfacial phenomena observed with their help. Discussion is illustrated by experimental results obtained for homopolymer mixtures with nuclear reaction analysis and secondary ion mass spectroscopy.

Key words: polymer blends, liquid thin films, ion beam analysis, composition vs. depth profiling techniques, miscibility conditions, surface segregation, wetting, phase separation

Razni pojavi na mejnih ploskvah kot so npr. soobstoj faz, površinska segregacija in omakanje na površini pa tudi s površino usmerjena ločitev faz, določajo mnoge lastnosti polimernih mešanic. Te pojave smo študirali na polimernih mešanicah (blendih) z geometrijo tankih plasti. Uporabljene so bile direktne tehnike profiliranja koncentracije z globino plasti, ki so bile razvite v zadnjem desetletju. Članek na kratko opisuje direktne metode profiliranja in pojave na mejnih ploskvah, ki smo jih opazovali s pomočjo omenjenih metod. V diskusiji so predstavljeni eksperimentalni rezultati homopolimernih mešanic z jedrsko reakcijsko analizo in sekundarno ionsko masno spektroskopijo.

Ključne besede: polimerne mešanice, tekoče tanke plasti, analiza z ionskimi snopi, tehnike profiliranja koncentracije z globino, pogoji mešljivosti, površinska segregacija, omakanje, ločitev faz

1 INTRODUCTION

Alloying polymers provides an inexpensive method to produce new materials with desired properties, often superior to either blend component alone¹. The spatial blend structure is rarely homogeneous. Compositional inhomogeneities are related with *internal* interfaces, separating coexisting phases inside the blend, and *external* interfaces exposed by the blend (**Figure 1**). The most complex situation occurs in blends confined in a thin film geometry.

Various phase domain morphologies are encountered in thin films, and exemplified in **Figure 1**. Their characterization precedes an enforcement of the proper performance of many low- and high- tech applications. The local concentration of the surface *segregation* 'cuticle' of one- phase layer (**Figure 1a**) is different from the composition in the bulk, modifying e.g. the surface wettability by paints. Complex 3- dimensional two- phase structure (**Figure 1b**), expected for the *separation* of polystyrene (PS)/ polybutadiene blends, results in very tough 'high impact PS'. The separation process can be directed by external surfaces leading to self- stratified films (**Figure 1c**), where individual domains have often different properties (e.g. gas permeation and mechanical characteristics in gas separation membranes).

Apart from these technology oriented aspects^{2,3}, the interfacial phenomena pose a fundamental scientific challenge to soft matter physics⁴. They can be catego-

rized according to complexity. The *internal* interface specifies miscibility conditions (Section 3a). These conditions, augmented by the knowledge of the specific segment interactions at given *external* interface, explain *surface segregation* (Section 3b). Finally, when all interfaces are treated explicit, the self- stratified films, created in the due course of *surface directed phase separation* (Section 3c), can be described.

Nowadays the spatial structure of blend films (phase morphology and local composition) can be determined with a nanometer precision, comparable with the polymer chain dimensions. Even the 3-dimensional complex morphology of two- phase systems can be resolved, e.g. with transmission electron microtomography⁵. The concentration vs. depth profiles $\phi(z)$ are examined by modern techniques⁶ yielding the volume fraction ϕ of the blend component(s) as the function of depth z within the thin film (**Figure 1**). Indirect profiling techniques, such as X-ray and neutron reflectivity, yield model dependent profiles $\phi(z)$ (although with excellent resolution $\delta = 1$ nm). To contrary, the straightforward profiles $\phi(z)$ are obtained with the commonly used *direct methods*⁶.

2 DIRECT PROFILING TECHNIQUES

The direct methods analyze the film composition with ion beams of medium (3-7 keV in dynamic Secondary Ion Mass Spectroscopy (SIMS)) or higher (0.7 - 7

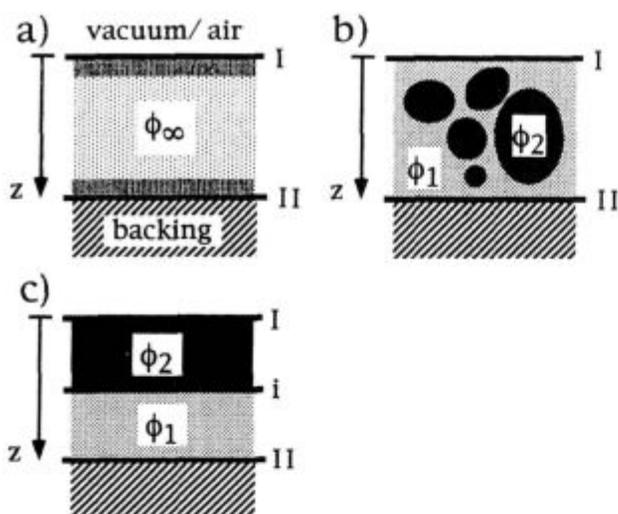


Figure 1: Thin polymer films composed of one phase ϕ (a), or two coexisting phases ϕ_1 and ϕ_2 (b, c) are not homogeneous. External interfaces I and II cause segregation (a), internal interface i separates coexisting phases (b and c)

Slika 1: Tanke polimerne plasti, sestavljene iz ene faze ϕ (a) ali iz dveh soobstoječih faz ϕ_1 in ϕ_2 (b, c), niso homogene. Zunanji mejni plasti I in II povzročita segregacijo (a), notranja mejna plast i ločuje soobstoječi fazi (b, c)

MeV) energy (Rutherford Back Scattering (RBS), Forward Recoil Spectrometry (FRES), Nuclear Reaction Analysis (NRA)).

Bulk of polymers are made up of elements which rarely provide an effective contrast for high energy techniques. RBS can in principle yield composition profiles of heavy elements present in polymers, but it is exceptionally used to trace polymers themselves⁶. This is because the labeling a polymer with a heavy element severely alters the extent of its mixing with other polymers. Therefore a deuterium labeling is commonly used instead, which allows for the profiling of 'stained' polymers in such methods as FRES and NRA. The deuterium 'staining' of one of the chemically distinct blend components introduces much smaller thermodynamic perturbation, visible only for longer chains, and easily evaluated⁷.

Non-resonant NRA⁸ is the high energy method of choice providing profiling deuterium in polymer films with the highest range (even of few microns) and best resolution ($\delta \sim 7$ nm at the free surface deteriorating to $\delta \sim 30$ nm at depth $z = 600$ nm). As a standard procedure thin polymer films are mounted on Si wafers (spin cast from solution either directly on Si, or cast on mica, floated on water, and picked up by Si backing bearing a precast film to form a multilayer if necessary), annealed at temperatures above polymer glass transition, and measured at room (or lower) temperature. The monoenergetic $^3\text{He}^+$ beam (with mm diameter) impinges on and penetrates into the thin film sample, as illustrated in **Fig-**

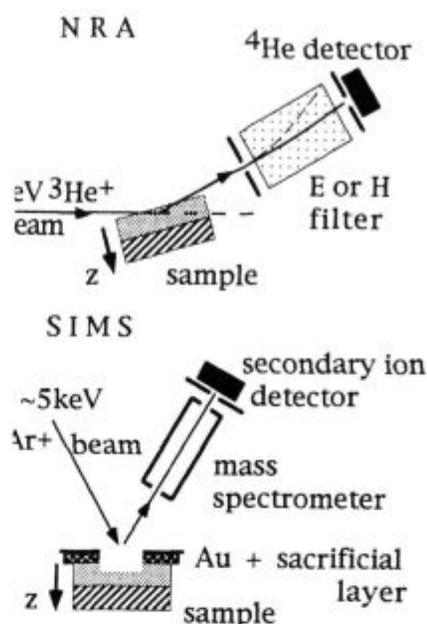


Figure 2: Schematic illustration of setups used to yield the composition ϕ vs. depth z profiles $\phi(z)$ in thin film samples with nuclear reaction analysis (NRA) (a) and dynamic secondary ion mass spectroscopy (SIMS) (b)

Slika 2: Shematska predstavitev priprav za merjenje koncentracije ϕ z globino z profila $\phi(z)$ v vzorcih tankih plasti z jedrsko reakcijsko analizo (NRA) (a) in dinamično sekundarno ionsko masno spektroskopijo (SIMS) (b)

ure 2a. At different depths z the reaction: $^3\text{He} + ^2\text{H} \rightarrow ^4\text{He} + ^1\text{H} + 18.4$ MeV takes place and the magnetic or electric filter allows only $^4\text{He}^+$ particles to reach the detector. The measured ^4He energy is related with the depth z , which can be calculated based on reaction kinematics and known energy losses of ^3He and ^4He in the sample. Finally, the correction of ^4He count rate with respect to the reaction cross section provides a relative profile $\phi(z)$ of the polymer 'stained' by deuterium. The absolute values of the volume fractions $\phi(z)$ are determined from the known (from preparation) overall amount of the deuterated material in the sample⁹, or by profiling the studied sample covered with an additional reference layer built of pure deuterated material¹⁰. Typical NRA profiles are shown in **Figures 3a and 4a**.

An alternative profiling method of dynamic SIMS^{11,12} is accomplished by monitoring individual atomic and molecular secondary ions emitted when the polymer sample is exposed to the primary ion (Ar^+ or another) beam with a medium energy (**Figure 2b**). The primary beam is scanned over an area of mm diameter, thereby eroding the sample and forming a flat crater with a growing depth. The secondary ions ejected from the central region of the crater are analyzed with mass spectrometer (with respect to their mass- to- charge ratio) and monitored as a function of the sputtering time. Prior to SIMS measurements, the polymer samples are covered by a polymer sacrificial layer and evaporated with Au. This is

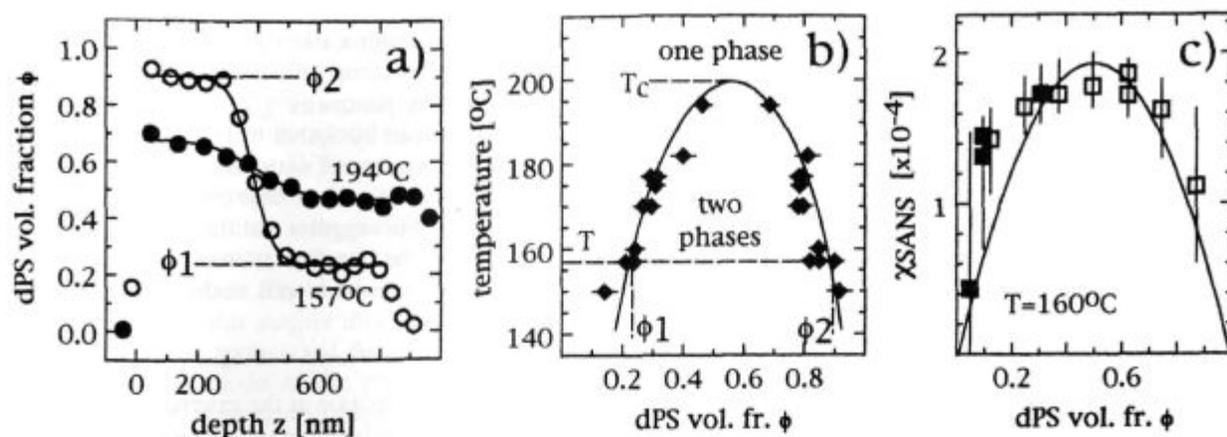


Figure 3: Relaxation of an initially sharp interface between pure polystyrene (PS) ($N = 27.8$ k) and pure deuterated polystyrene (dPS) ($N = 9.2$ k) leads (here after a month long annealing at varied T) to coexisting profiles $\phi(z)$ (a). NRA profiles, tracing local dPS concentration, determine coexisting compositions, ϕ_1 and ϕ_2 , used to plot experimental phase diagram (b). This is well fitted by theory (see solid line in b) to yield the specific form of segmental parameter $\chi_{SANS}(\phi)$ presented (for $T=160^\circ\text{C}$) in (c) as a solid line. The $\chi_{SANS}(\phi)$ values measured by SANS for bulk blends of PS ($N = 15.4$ k)/dPS ($N = 11.5$ k) and PS ($N = 8.7$ k)/dPS ($N = 11.5$ k) are marked in (c) as open and solid symbols, respectively

Slika 3: Relaksacija na začetku ostre mejne površine med čistim polistirenom (PS) ($N = 27,8$ k) in čistim deuteriranim polistirenom (dPS) ($N = 9,2$ k) vodi (tu po enomesečnem kondicioniranju pri različnih T) do soobstoječih profilov $\phi(z)$ (a). NRA profili, ki spremljajo lokalno dPS koncentracijo, določajo soobstoječe sestave, ϕ_1 in ϕ_2 , so bili uporabljeni za eksperimentalni fazni diagram (b). Ta se dobro ujema s teorijo (neprekinjena črta v b), tako da dobimo specifično obliko segmentnega parametra $\chi_{SANS}(\phi)$, ki je prikazan (pri $T = 160^\circ\text{C}$) v (c) kot neprekinjena črta. Vrednosti $\chi_{SANS}(\phi)$, izmerjene s SANS za polimerne mešanice v masi, so pri (c) označene z odprtimi simboli za PS ($N = 15,4$ k)/dPS ($N = 11,5$ k) in s polnimi simboli za PS ($N = 8,7$ k)/dPS ($N = 11,5$ k)

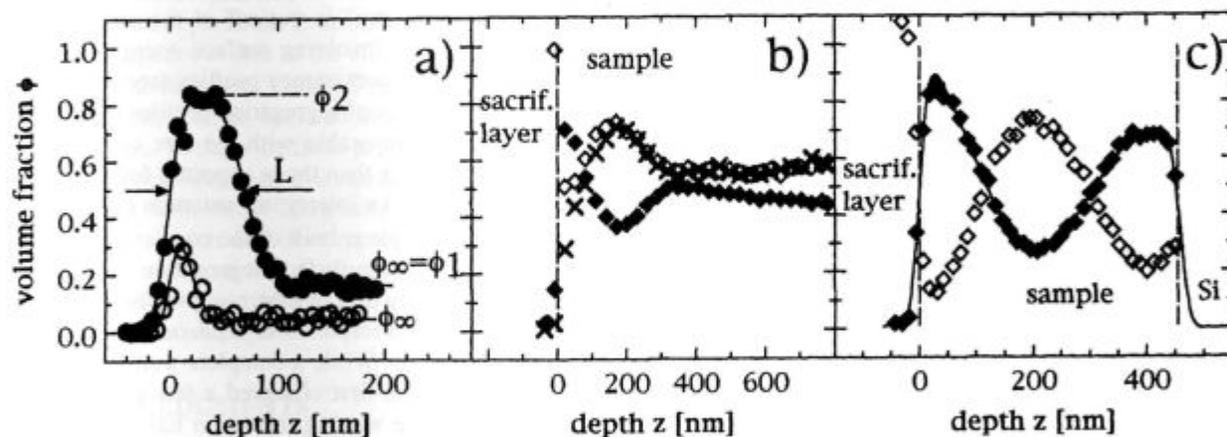


Figure 4: (a) NRA profiles $\phi(z)$ of the surface exposed by the mixture of random olefinic copolymers $[(C_4H_8)_{1-x}(C_2H_3(C_2H_5))_x]_N$: a hydrogenous h52 ($x=52\%$, $N=1510$) and a partly deuterated d66 ($x=66\%$, $N=2030$), after a few hours of annealing at $T=99^\circ\text{C}$. The open and solid symbols correspond to the surface enriched in d66 and completely wetted by the d66-rich phase ϕ_2 , respectively. (b and c) SIMS profiles $\phi(z)$ illustrating surface phase separation. Its initial stages were recorded (see b) for the blend of dPS ($N = 6.4$ k)/ brominated polystyrene PBr_xS ($N=1.7$ k, $x=0.08$) annealed for 1 day at $T=180^\circ\text{C}$. Its late stages (see c) were observed in the blend of dPS ($N=17.4$ k) / PS ($N=27.8$ k) annealed for 20 days at $T=190^\circ\text{C}$. (Br, $^1\text{HC}/\text{C}$ and $^2\text{HC}/\text{C}$ profiles are marked by crosses, open and solid symbols, respectively)

Slika 4: (a) NRA profili $\phi(z)$ za površine, ki so bile izpostavljene zmesi naključnih olefinskih kopolimerov $[(C_4H_8)_{1-x}(C_2H_3(C_2H_5))_x]_N$: vodikov h52 ($x=52\%$, $N=1510$) in delno deuterirani d66 ($x=66\%$, $N=2030$) po nekaj urah kondicioniranja pri $T=99^\circ\text{C}$. Odprti simboli ustrezajo površini, ki je obogatena z d66 in polni simboli površini, ki je popolnoma omočena z d66 - bogato fazo ϕ_2 . (b in c) SIMS profili $\phi(z)$ predstavljajo s površino usmerjeno ločitev faz. Začetne stopnje so posnete (glej b) za polimerno mešanico dPS ($N=6,4$ k) / bromirani polistiren PBr_xS ($N=1,7$ k, $x=0,08$), ki je bila kondicionirana en dan pri $T=180^\circ\text{C}$. Kasnejše stopnje (glej c) so prikazane za polimerno mešanico dPS ($N=17,4$ k) / PS ($N=27,8$ k), ki je bila kondicionirana 20 dni pri $T=190^\circ\text{C}$. (Br je označen s križci, $^1\text{HC}/\text{C}$ z odprtimi simboli in $^2\text{HC}/\text{C}$ s polnimi simboli)

to obtain a steady sputtering state before the real sample is reached by primary ions, and to avoid charging effects, respectively. Sputtering rates are determined by NRA (FRES or ellipsometric) measurements of selected control samples. This allows us to evaluate the absolute depth scale for each sample. The very good depth resolu-

tion of $\delta = 5$ nm, which deteriorates only slightly with depth z , is the one of two main SIMS advantages. The simultaneous profiling of various species such as ^1H , ^2H , C, O, Br, Si, N, etc., labeling polymers or present in the sample, is the second virtue. Most of these species are detected however only in semi-quantitative fashion. It

has been concluded that the absolute local concentrations $\phi(z)$ can be determined for polymers 'stained' with deuterium (based on the ^2H - ^1H or relative $^2\text{HC}/\text{C}$ - ^{12}C signals). The concentration calibration seems to hold also for hydrogenous (traced by $^1\text{HC}/\text{C}$) and for brominated (monitored by Br) polymers¹² (see **Figure 4b**). Typical SIMS profiles are shown in **Figures 4b and c**.

3 INTERFACIAL PHENOMENA IN THIN FILMS

3.a Phase coexistence

Two different polymer chains composed of N ($\approx 10^3$) segments would mix, when a gain in the entropy of mixing outweighs unfavorable interaction χ between unlike polymer segments¹. Entropy of mixing scales as $1/N$, and therefore the critical interaction χ_c necessary to cause the phase separation is $1/N$ times smaller as compared to simple liquid ($N=1$) alloys. In most cases χ , related with different cohesive energy of blend components, reduces with temperature as $1/T$. Therefore homogeneous one-phase mixture is expected (see **Figure 3b**) at higher temperatures ($T > T_c$), while two adjacent macroscopic phases (ϕ_1 and ϕ_2) are expected to coexist in thermodynamic equilibrium at temperatures below critical point ($T < T_c$). The balance of three factors, related with the entropy of mixing, the segment-segment interaction and the configurational entropy of polymer coils, determines the composition profile $\phi(z)$ across the internal interface⁴. As the temperature is elevated the interfacial width increases and diverges to infinity for a miscible blend at $T > T_c$.

Until recently the phase coexistence of high polymer mixtures have been evaluated with a dynamic method determining cloud-point loci or with Small Angle Neutron Scattering (SANS). While the first technique is problematic due to extremely low molecular mobility, the second one measures the segmental interaction χ_{SANS} away from coexistence curve. A new direct approach has been developed^{13,14} in which the profiles $\phi(z)$ are measured (for different T) across the internal interface between two coexisting phases forming a bilayer morphology as in **Figure 1c**. Such samples are obtained from bilayers composed of pure blend components as a result of an annealing process, involving the relaxation of the initial sharp internal interface and a material transport across the interface.

Figure 3a presents the exemplary coexistence profiles obtained with this novel method for the isotopic PS blend¹⁴. The corresponding coexistence curve presented in **Figure 3b** shows $T_c = 197^\circ\text{C}$, which is much elevated as compared to $T_c = 0.9^\circ\text{K}$ characterizing the isotopic mixture of simple liquids ^3He and ^4He . While unfavorable segment-segment interaction is comparable in both cases, the mixing entropy is reduced only for the isotopic PS blend. The question of accordance between the coexistence conditions determined by the novel approach^{13,14} involving thin submicron films, and evaluated by SANS

for bulk samples (with a size of c.a. 1 mm) is addressed by **Figure 3c**. The composition dependence of the segmental interaction parameter χ_{SANS} for the isotopic PS mixtures determined by SANS¹⁵ (and marked by points) is in very good agreement with that (denoted by a solid line) based on the thin films data corresponding to **Figures 3a and b**. This suggests that the coexistence conditions yielded by the interface relaxation method should be valid also for polymer blends in the bulk.

3.b Surface segregation and wetting

The local concentration at the external surface differs usually from the constant concentration ϕ_∞ of one-phase in the bulk of the sample¹⁶. This is demonstrated in **Figure 4a** for the free surface of an olefinic blend¹⁷. The reason for this *surface segregation* (or *enrichment*) is the specific surface interaction of polymer segments, lowered when the surface blend concentration is changed. The amount of the segregation is a result of a trade-off between this specific surface energy f_s and the bulk term, expressing the free energy of mixing (three factors mentioned in Section 3a) and opposing the segregation. For known bulk concentration ϕ_∞ the segregation profile $\phi(z)$ is generated by the bulk energy term, specified by coexistence conditions. $\phi(z)$ is cut off at the surface by a boundary condition involving surface energy f_s ⁴. Similarly to the case of coexistence profiles (see **Figure 3a**) also the spatial scales of segregation profiles (see **Figure 4a**) are at least comparable with the size of a polymer coil, and much larger than those expected for simple liquid (metal) alloys. An interesting situation occurs when the bulk of the sample is built of the coexisting phase ϕ_1 . The thickness L of the surface segregation layer can be then microscopically thin or macroscopically thick (as in **Figure 4a**). This corresponds to a *partial* and *complete wetting*, respectively. While a complete wetting for polymer blends has been first observed a few years ago¹⁸, a partial- to complete wetting transition has just been reported¹⁹.

According to a conventional view point the surface of the polymer mixture is enriched in the component with lower cohesive energy, regardless of the value of the composition ϕ_∞ in the bulk of the sample. This is not necessary true. First, entropy- related forces driving the segregation have been concluded²⁰ besides those related to cohesive energy difference. Second, an *enrichment-depletion duality* has been advocated by theory²¹ and computer simulations²², and just observed in real polymer blends²³. The surface is *enriched* in one blend component when the bulk composition is below a certain value $\phi_\infty < Q$, and it is *depleted* in this component for larger bulk concentration $\phi_\infty > Q$.

3.c Surface directed phase separation

A binary mixture is thermodynamically unstable when its average composition corresponds to the two-

phase region bounded by a spinodal curve. In such conditions spontaneous bulk- and surface- driven phase separations occur. The bulk separation, driven by thermal fluctuations, results in composition waves with random directions and phases. Different scenario is expected when a surface segregation is observed. Then a concentration gradient, created at the surface, induces composition waves propagating with a fixed phase in a direction normal to the surface. The concentration oscillation $\phi(z)$, characteristic for this *surface directed phase separation*, extends from the surface and decays inside the sample, where the bulk mode of the phase separation dominates²⁴. This is presented in **Figure 4b** for the mixture composed of deuterated and brominated PS¹². Finally, at the late stages of this process, a stratified plate morphology can be obtained²⁵ as presented in **Figure 4c** for the isotopic PS mixture. This layered structure can be controlled in a tunable fashion by a surface active copolymer admixed to the polymer blend²⁵.

4 CONCLUSIONS

Binary polymer blends are usually incompatible or only partly compatible. Already very weak interactions between unlike segments, as in isotopic mixtures, would lead to phase separation. Even miscible polymer 'alloys' are inhomogeneous due to the effects related with an external blend interface. Ordered segregation and separation processes can be initiated at the external interfaces of thin films. To describe them properly coexistence conditions needed first to be evaluated. Nowadays thin films are studied with direct composition vs. depth profiling techniques, which are best represented by SIMS and NRA. The advent of real 3- dimensional profiling is expected, which would enable to study directly complex two- phase morphologies.

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