

Identification of the morphology of a thin film by fluorescence laser-scanning confocal microscopy

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This study is an extension of our previous paper (Hayashi, M. *et al.* *Polymer*, 1998, **39**, 299) dealing with the phase separation and structure formation of a polysulfone (PSU)/polyamide (PA) blend as observed by laser scanning confocal microscopy (LSCM) and scanning electron microscopy (SEM). Here we use fluorene-labelled PSU in order to apply fluorescence LSCM for more detailed morphological investigations of the internal structure of a thin film as-cast from solution. © 1998 Elsevier Science Ltd. All rights reserved.

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Introduction

Recently we presented a structural investigation of a novel high-temperature stable polymer blend of a polysulfone and a polyamide by laser scanning confocal microscopy (LSCM) combined with scanning and transmission electron microscopy (SEM/TEM)¹. The surface structure of a thin film cast on to a glass slide was studied by LSCM in reflection mode, and in combination with scanning electron microscopy (SEM) and element-dispersive X-ray analysis (EDX), the different phases could be identified. As long as one is only interested in the topology, the LSCM reflection mode studies are sufficient, but if one wants to study the interior morphology of such a thin film the contrast is too poor. In order to examine the structure beneath the surface, especially the contact area of the two polymers to the glass substrate, we extended our studies by using a fluorene-labelled PSU which allows us determine the location of the PSU by detecting the fluorescence emission by LSCM.

Experimental

The fluorene-labelled polysulfone has an average molecular weight (M_w) of 6.8×10^3 and a glass transition temperature (T_g) of 179°C. *Scheme 1* shows the structure of the polymer where 0.14 mol.% of the bisphenol-A units are replaced by 9,9'-bis-(4-hydroxyphenyl)-fluorene units. Details about the synthesis are given elsewhere^{2,3}. The amorphous PA (see *Scheme 2*)⁴ has an average molecular weight (M_w) of 1.4×10^4 and has a T_g of 130°C.

For blending, the two polymers were dissolved in *N*-methyl pyrrolidone (NMP), which is a good solvent for both components. A few drops of the about 1 wt.% solution having a composition of PSU/PA (70/30, wt./wt.%) were put onto a glass slide and the solvent was allowed to evaporate at 90°C under vacuum for 5 min. The thus obtained film was annealed at 290°C for 30 min.

LSCM was performed with a Zeiss LSM 320 using an Ar

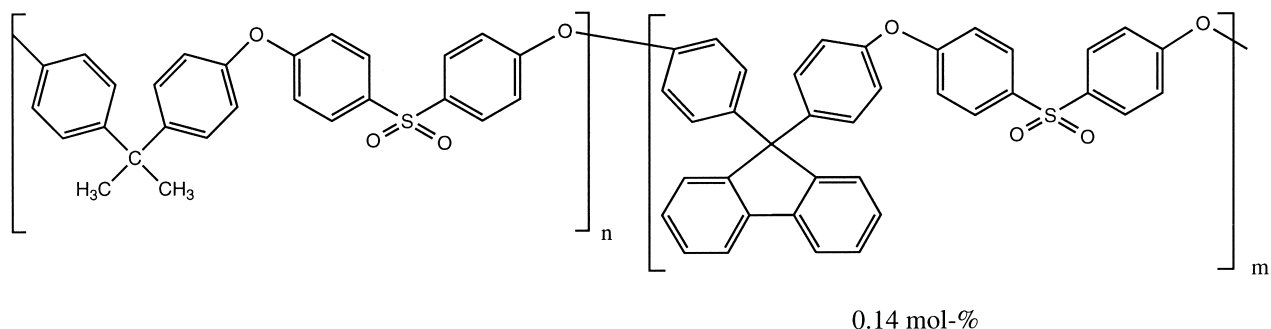
laser with $\lambda = 488$ nm which corresponds to the excitation wavelength of the fluorene label. The emission maximum of the label is about $\lambda = 510$ nm.

Results and discussion

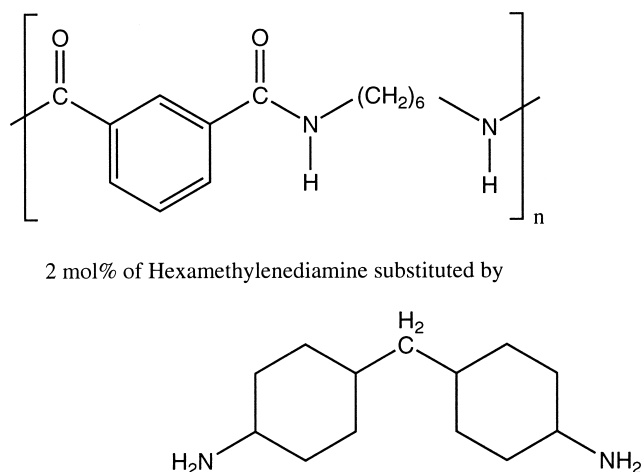
Figure 1 shows the reconstruction of the polymer–air interface obtained by LSCM in reflection mode. A series of 30 sliced images was recorded, each with a focal depth of about 500 nm and a distance of 500 nm apart from each other along the depth direction. From the location with strongest intensity, the shape of the polymer–air interface was obtained. The surface undulation reflects the maximum of the reflected light captured by LSCM. From these reflection mode studies in the LSCM, we can only judge the topology of the thin film specimen which only indirectly reflects information about the interior structure of such a thin film, i.e., phase-separated structure. The reflection of the incident laser beam of the polymer–air interface at the border regions of the protruding domains is controlled by the orientation of the interface, i.e., angle of the interface normal relative to the incident beam. As visible in *Figure 1*, the domains are surrounded by a valley. This valley is caused by an artifact generated by the increasing angle, and therefore less light will be reflected in the direction to the detector⁵ (see also *Figure 4*).

Figure 2 shows the reflection obtained from the polymer–air interface, i.e., the white line marked as (air–surface). Part *a* shows a single slice with a focal depth of about 500 nm as observed at the polymer–air interface (as). Parts *b* and *c* are cuts along the *x,z*- and *y,z*-planes marked by black lines in part *a*. *Figure 3* shows the image obtained with the fluorescence of the fluorene label. Part *a* shows a single slice with a focal depth of about 500 nm as observed directly at the polymer–air (as) interface. As in *Figure 2*, parts *b* and *c* are cuts along the *x,z*- and *y,z*-planes marked by white lines in part *a*. We can clearly see that the PSU, which contains the fluorene, is forming a bowl-like structure and the top is sticking out of the polymer–air interface about 1 μ m. The dark area showing no intensity corresponds to the polyamide matrix, which shows a smooth surface parallel to

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Scheme 1



Scheme 2

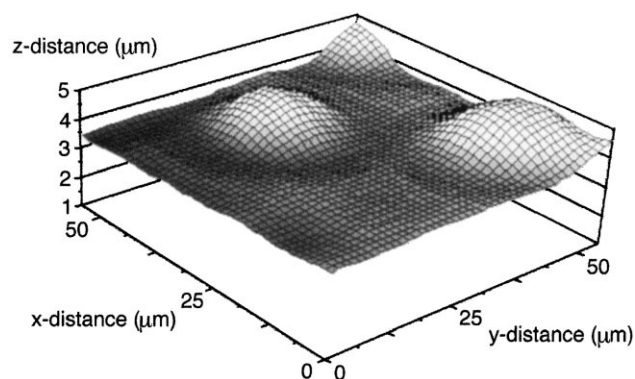


Figure 1 Shape of the interface the air-surface observed for a thin film of a blend of fluorene-labelled PSU and PA. The film was prepared by solution casting and subsequent annealing at 290°C for 30 min. The image was reconstructed from the reflection of the polymer-air interface in the LSCM (corresponding to Figure 2a). The height at the maximum of the protruding phase is about 1 μm

the surface of the glass slide. The schematic illustration of the structure formation of the two polymers is given in Figure 4.

The bright rings observed in the reflection mode in Figure 2 are probably caused by interference of the incoming laser light with the thin film sample⁶. At the moment we do not have a concrete explanation for the dark (marked D) and bright rings (marked B) in the x,y - and x,z -plane in Figure 3 observed around the periphery of the PSU

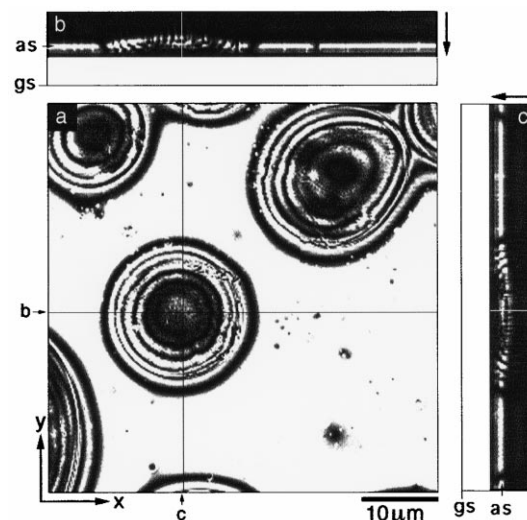


Figure 2 Reflection image obtained with reflected light from the polymer-air interface (air-surface) of a thin film described in Figure 1. Part a is a single slice with a focal depth of 500 nm as obtained at the film surface. The lines (b) and (c) in part a show the cutting directions where the images in the x,z -plane (part b) and y,z -plane (part c) were obtained; gs is the glass surface and the scale bar attached to the figure is common for the images in parts a-c

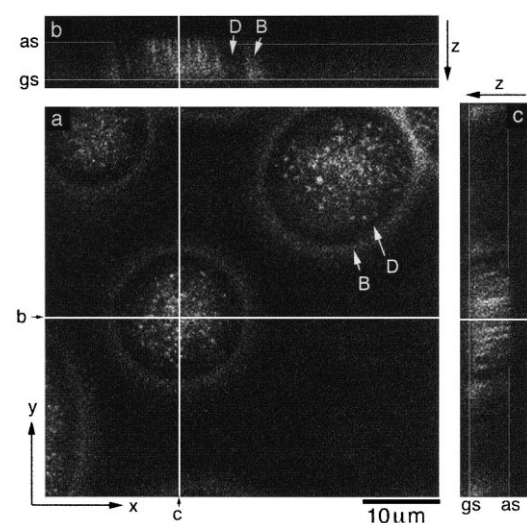


Figure 3 Fluorescence LSCM with the fluorene label of the PSU; the bright area corresponds to the PSU. The PA forms the matrix showing no fluorescence and thus appears dark in parts a-c. Part a is a single slice with a focal depth of 500 nm as obtained in the middle of the film, i.e., 2.5 μm beneath the film surface. Lines (b) and (c) show the cutting directions where the images in the x,z -plane (part b) and the y,z -plane (part c) were obtained

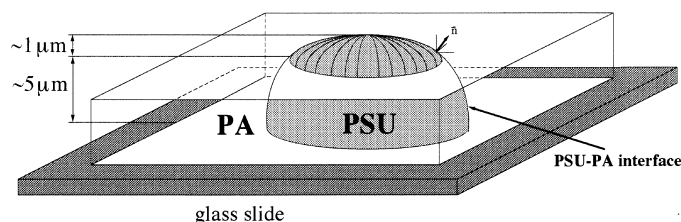


Figure 4 Schematic illustration of the morphology of the thin film of a blend of fluorene-labelled PSU and PA

domains. This interesting pattern only allows a speculative interpretation^{7,8} at the moment and a further exploration should be done in future.

As mentioned above we succeeded in visualizing the internal structure of a thin blend film of fluorene-labelled PSU and PA. This was not possible in our previous experiment¹ where we used a blend of pure PSU and PA. The surface structure, i.e., the shape and size of the protruding PSU-phase, is the same as we observed with the unlabelled blend and the fluorene label does not affect the surface topology and therefore probably not the structure of the blend film. Therefore, the fluorene labelling should not affect the miscibility of PSU and PA. Since the PSU and PA are highly immiscible, it may be reasonable to assume that a minor modification of PSU with the fluorene label would not affect their miscibility very much.

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8. For the interested reader we want to offer a speculative interpretation which shall motivate further discussion: the bright ring (B), i.e., fluorescence caused by the fluorene-labeled PSU, is caused by the following mechanism. Owing to the high annealing temperatures, the fluorene-labeled PSU and the PA are able to react at their interface to form a block copolymer. This might possibly be because the fluorene-labeled PSU still contains chlorine and hydroxy end groups which can react with the amino end groups of the PA at very high temperatures. This block copolymer is mainly located at the interface and will stay there during further annealing. Owing to the particular preparation method employed for the fluorene-labeled PSU, it still contains a certain amount of unlabeled PSU. Therefore the PSU phase itself might undergo phase separation to form a morphology which causes the contrast visible on the LSCM image in *Figure 3*.