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Notes

Interdiffusion of Thin Polymer Layers Studied by External Reflection Infrared Spectroscopy

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Introduction

Polymer interdiffusion can be studied through analysis of the interface between two polymers, using techniques such as small-angle X-ray scattering[1] and small-angle neutron scattering[2] for systems where one component has been dispersed in the other and Rutherford backscattering,[3] forward recoil spectroscopy,[4] secondary ion mass spectroscopy,[5] neutron reflection,[6] infrared microdensitometry,[7] and ATR-infrared spectroscopy[8] for bilayer samples. For these bilayer systems we have used an external reflection IR technique, evaluating the experimental spectra by comparison with simulated spectra of mixed and unmixed systems.

Experimental Section

Sample Preparation. Bilayer samples were prepared by floating a spin-coated PVC ($M_w = 55 \times 10^3$, $M_n = 30 \times 10^3$) film off onto water, picking it up with a PMMA ($M_w = 100 \times 10^3$, $M_n = 45 \times 10^3$) film spin-coated on a gold or glass substrate, and drying the bilayer overnight at 70 °C in vacuo. The PVC and PMMA were allowed to interdiffuse at 150 °C. External reflection IR spectra using an incidence angle of 80° were recorded on a Bruker IFS88 spectrophotometer equipped with a narrow-band MCT detector with 4-cm^{-1} resolution and were referenced against the reflection spectrum of a bare glass or gold substrate.

Infrared Spectral Simulations. For the determination of the optical constants the following procedure was followed: the imaginary part of the refractive index was calculated from cast films on KBr, the absolute values being determined by comparison with free-standing films whose thicknesses were calculated from the interference fringes. The values used for the n_∞ were taken from the literature.[9] The real part of the refractive index was calculated from the imaginary part by a Kramers–Kronig transformation. For this Kramers–Kronig transformation a numerical integration was performed based on MacLaurin's formula using a 1-cm^{-1} step size between the data points.[10] Ohta and Ishida[10] reported obtaining the most accurate results using this procedure. The optical constants for PMMA and PVC determined this way agree very well with those reported by Graf et al.[9] For layers consisting of a mixture of PMMA and PVC additivity of the optical constants of the materials was assumed—i.e., the polymers were assumed not to affect each other's IR spectra—and densities of mixtures were taken to be linear interpolations of the densities of both components. Vorenkamp et al. could not find shifts of PMMA or PVC vibrations upon mixing PMMA and PVC,[11] and transmission spectra showed that the optical constants of blends of PMMA and PVC were linear additions of the optical constants of the pure components.

Spectra of systems consisting of a number of parallel layers were simulated by using the matrix multiplication procedure suggested by Abelès.[12] The refractive index of gold was assumed to be $9.5 - 30i$[13] over the entire IR range studied; for glass the real part of the refractive index was centered at 1.5.

Results and Discussion

Taking gold as a substrate and the "normal" external reflection setup using light polarized parallel to the plane of incidence, one can observe small differences between the simulated spectrum of the double layer of PMMA and PVC and the spectrum of the one-layer mixture with the corresponding volume ratio (not shown). Upon mixing, the PMMA carbonyl absorption band shifts 4 cm^{-1} to the lower wavenumber side, and the ratio of intensities of the strong PMMA bands at 1196 and 1154 cm^{-1} changes significantly. These changes can be attributed to a decrease in the optical distortion effects in the mixture, which were responsible for a shift of the carbonyl stretching vibration to higher wavenumbers and an increase of the 1196/1154-cm^{-1} absorption ratio. The absorption coefficients of PMMA in the mixed layer are lower than those of a pure PMMA layer because of the "dilution" of the strongly absorbing PMMA with PVC, and, as a consequence, the variation of the real part of the refractive index across the absorption band is less pronounced. The experimental spectra for this setup were completely identical with the calculated spectra.

With s polarization (perpendicular to the plane of incidence), the standing-wave pattern of the electrical field intensity, resulting from interference of the incoming and reflected beams, has a node on the gold substrate due to destructive interference. Therefore very thin films will not absorb IR radiation significantly, which is the reason why external reflection experiments with s polarization are not commonly used for practical purposes. With increasing distance from the substrate, however, the electrical field intensity will increase, and films of several tenths of a micron thickness will absorb IR radiation, the parts of the film furthest away from the substrate contributing most strongly. The wavelength of this standing wave decreases with increasing wavenumber, and therefore the electrical field intensity increases faster with distance from the substrate at higher wavenumbers, a phenomenon that is illustrated by the high absorbances of the C–H stretching vibrations around 2900 cm^{-1} relative to the absorbances at lower wavenumbers (Figure 2). The simulated spectra show increasing intensities of the carbonyl and PMMA C–H stretching vibrations at 1730, 2948, and 2996 cm^{-1} (Figure 1) upon mixing, an effect that is also observed experimentally upon annealing two layers of PMMA and PVC (Figure 2) at 150 °C for several hours. The diffusion of PMMA away from the substrate into the higher electrical field intensity region of the standing wave is responsible for the enhancement of PMMA absorption bands. The spectra taken after 2 and 3 h of annealing (Figure 2D,E) are identical, and the intensity of the carbonyl peak at 1730 cm^{-1} equals the calculated intensity of the carbonyl peak of the mixture (Figure 1B), suggesting that the interdiffusion of this system is complete after 2 h.

For external reflection experiments on a glass substrate the physical effects, resulting from reflections, are less

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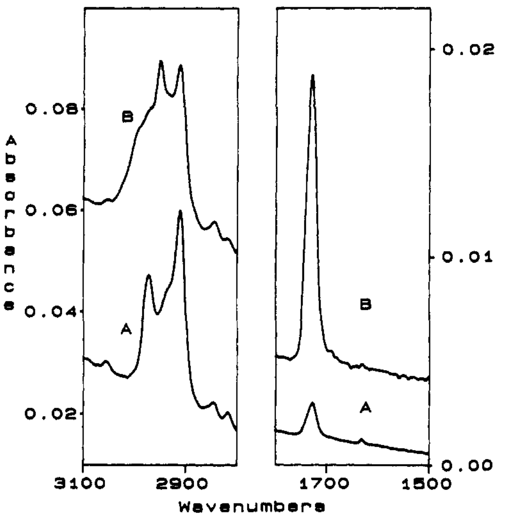

Figure 1. Simulated external reflection IR spectra with s polarization of (A) a bilayer of 0.15-μm PMMA and 0.43-μm PVC on gold and (B) a 0.58-μm layer of mixed PMMA/PVC (15/43 v/v).

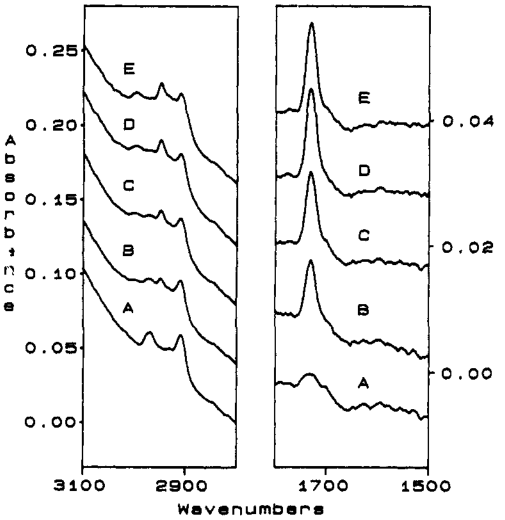

Figure 2. Experimental external reflection IR spectra with s polarization of a bilayer of 0.15-μm PMMA and 0.43-μm PVC on gold after (A) 0, (B) 0.5, (C) 1, (D) 2, and (E) 3 h of annealing at 150 °C.

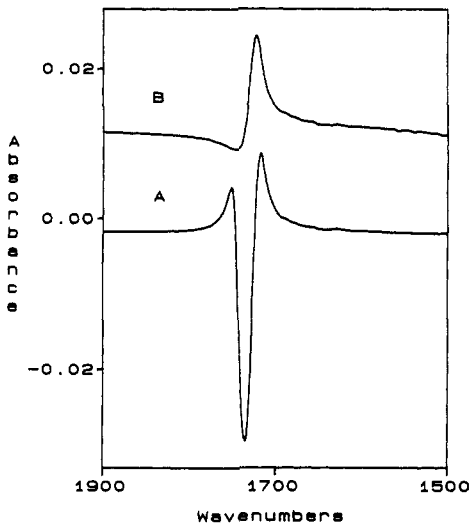

Figure 3. Simulated external reflection IR spectra with p polarization of (A) a bilayer of 0.15-μm PMMA and 0.43-μm PVC on glass and (B) a 0.63-μm layer of mixed PMMA/PVC (15/48 v/v).

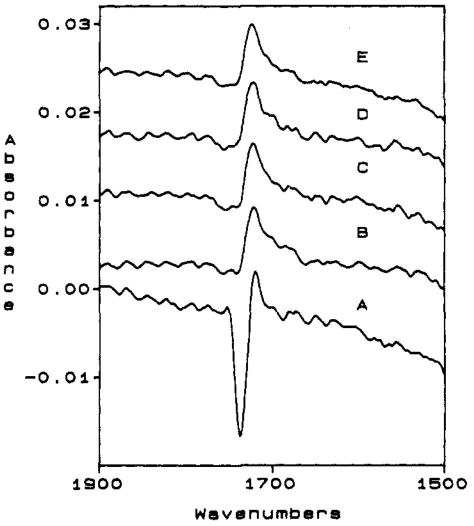

Figure 4. Experimental external reflection IR spectra with p polarization of a bilayer of 0.15-μm PMMA and 0.48-μm PVC on glass after (A) 0, (B) 0.5, (C) 1, (D) 2, and (E) 3 h of annealing at 150 °C.

obvious, and an interpretation as straightforward as in the case of a gold substrate cannot be given easily. Although the intensity of the reflected light is not as high as for metallic substrates (24 and 54% for parallel and s-polarized light, respectively), absorption spectra can be obtained. For a PMMA–PVC double layer the spectrum with s-polarized light does not change significantly upon mixing and is therefore not shown. On the other hand, differences between mixed and unmixed systems with p-polarized light are calculated to be significant (Figure 3). In Figure 4 it can be seen that PMMA/PVC interdiffusion on glass substrates can be studied by this method. We have only shown the carbonyl region because this region exhibits the largest effect and because the region below 1400 cm^{-1} is strongly affected by glass absorptions. The spectra using this setup did not change significantly after annealing for periods over 30 min. The observation that for a glass substrate and p polarization the spectral changes due to interdiffusion seem to be completed after 30 min, whereas for a gold substrate and s polarization, spectral changes are visible up to 2 h, is probably only due to the fact that the two methods have different sensitivities for the position and shape of the interdiffusion profile. This was also suggested by spectral simulations of interdiffusion profiles, describing subsequent stages of an interdiffusion process, which indicated that a glass substrate with p-polarized light was more sensitive to early stages of interdiffusion and a gold substrate with s-polarized light more to later stages, as we will publish in the near future.

More details of the interdiffusion process, e.g., the interdiffusion profile, may be elucidated by studying PMMA/PVC bilayers of different thicknesses (and thickness ratios) and different substrates with variable angles of incidence. Diffusion profiles (modeled by a large number of thin parallel films with a stepwise changing composition) are currently being simulated; density variations can also be taken into account. Other systems studied in our laboratory include the interdiffusion of PVC with PMMA grafted on a glass slide and self-diffusion of deuterated PMMA with (grafted) hydrogenated PMMA. Also ATR interdiffusion studies reported by Vorenkamp et al.[8] can be evaluated quantitatively with this simulation approach.

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Registry No. PMMA, 9011-14-7; PVC, 9002-86-2.