Spectroscopic monitoring of phase separation in polymer blends

G. C. Eastmond* and S. V. Kotomin†
Chemistry Department, Donnan Laboratories, Liverpool University, Liverpool L69 3BX, UK
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Phase separation in polymer blends has been monitored by u.v. absorption spectrophotometry. An 'absorption' peak forms in the early stages of phase separation and moves to longer wavelengths and broadens as the morphology ripens. This method may provide a useful alternative to scattering techniques to monitor phase separation.

(Keywords: polymer blends; phase separation; u.v. spectroscopy)

The development of phase separation in polymer blends and changes in morphology are widely studied by light scattering and other scattering techniques[1]; most workers examine the angular dependence of the scattered intensity using monochromatic radiation. Scattering decreases the intensity of the transmitted beam and cloud points are widely used to identify the onset of phase separation when determining phase diagrams. However, it has previously been noted that the onset of turbidity in the early stages of phase separation in polymer blends is dependent on the wavelength of the transmitted light used[2].

In our earlier determinations of phase diagrams for several polymer blends, by monitoring decreases in optical transmittance on phase separation, we also realized that the determination of 'cloud points' for many systems is system specific and in every case it is necessary to specify the spectral characteristics of the light used.

In this preliminary communication we report new observations on the changes in the u.v.–visible light absorption spectra that occur during the process of phase separation in some polymer blends.

Two polymer systems were used in this study: (i) polystyrene–poly(vinyl methyl ether) (PS–PVME) and (ii) bisphenol-A polycarbonate–poly(methyl methacrylate) (PCA–PMMA). Polymers with the following molecular weights were obtained from Aldrich: PS, 45 000; PVME, 33 000; PCA, 25 000; PMMA, 74 000 g mol^{-1}. U.v.–visible spectra were recorded with the aid of a Hewlett–Packard HP8452 diode-array spectrophotometer in the range 190–820 nm with an integration time of 1 s. Thin (~0.01 mm thick), transparent polymer films were cast from solutions in toluene (for PS–PVME) and tetrahydrofuran (for PCA–PMMA) on silica plates. The sample preparation procedures adopted are known to produce homogeneous polymer mixtures[3,4]. Phase separation was induced by isothermal heating of the samples on a Mettler FP-52 hot stage.

Figure 1 shows the evolution of the absorption spectra during heating and phase separation for two polymer blends: (i) 30% PC + 70% PMMA and (ii) 40% PS + 60% PVME. As observed from the spectra, before phase separation both polymer blends under investigation have absorption maxima in the near-u.v. region. These peaks arise from the absorption of u.v. light by chromophores in the constituent polymers.

During phase separation, some notable changes take place. For both blends a second peak appears at about

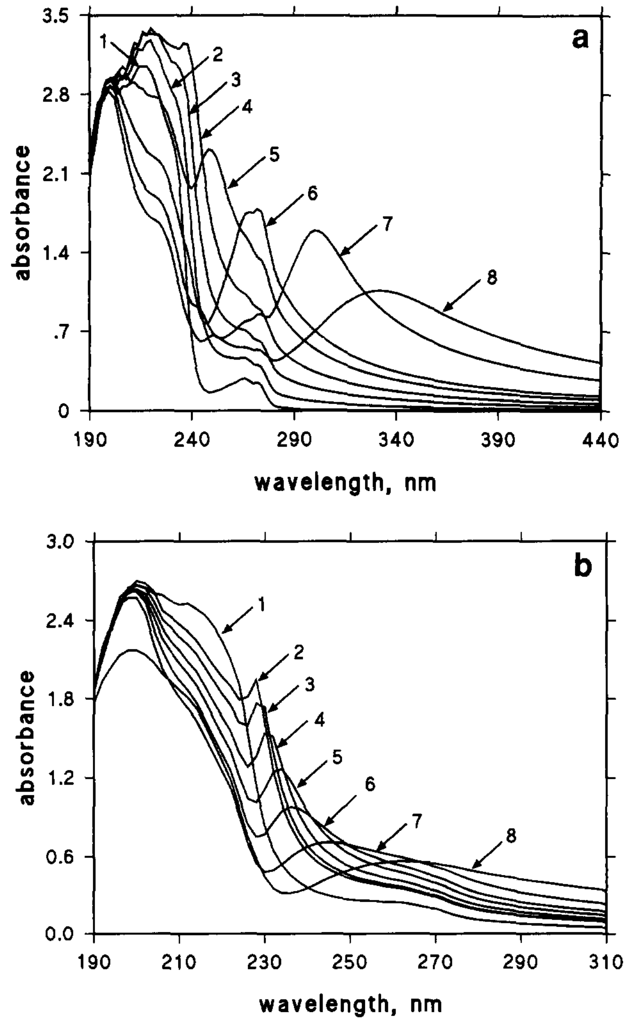

Figure 1 Absorption spectra for polymer blends: (a) PC–PMMA at 200°C; (b) PS–PVME at 100°C. Absorption spectra are of the homogeneous blends and of phase-separated blends at specified heating times after initial phase separation: 1, before phase separation; 2, 1 min; 3, 2 min; 4, 5 min; 5, 10 min; 6, 20 min; 7, 40 min; 8, 80 min

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* To whom correspondence should be addressed

† Permanent address: Institute of Petrochemical Synthesis, Russian Academy of Sciences, Moscow 117912, Russia

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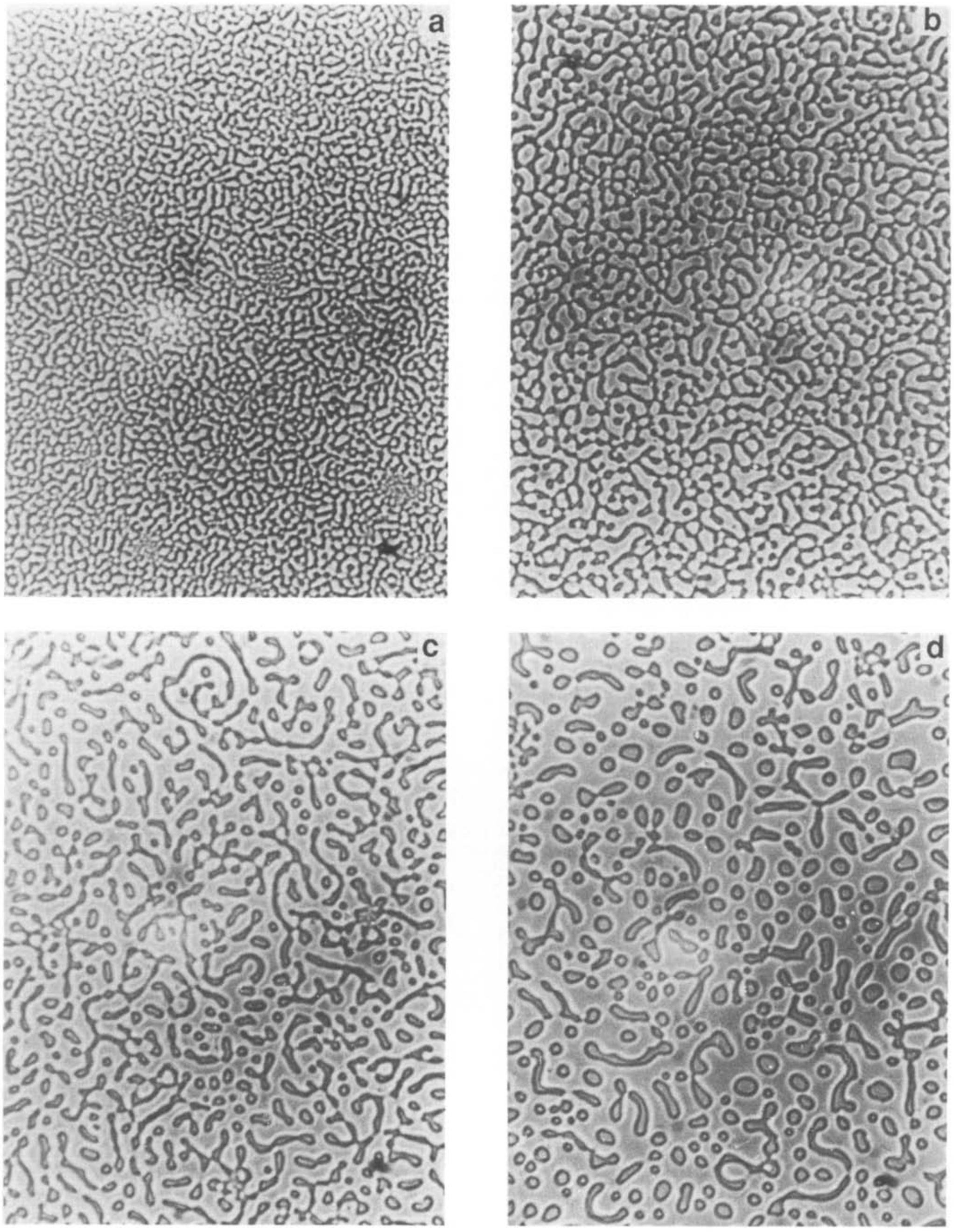

Figure 2 Evolution of the morphology of a 30:70 (wt/wt) PC–PMMA blend; times specified are heating times at 200°C after initial phase separation: (a) 5 min; (b) 10 min; (c) 20 min; (d) 40 min

230–240 nm and this peak gradually moves to longer wavelengths, although the samples contain no chromophores that absorb at those wavelengths. This phenomenon is associated with the development and growth of phase-separated domains in the blends, as we have observed in parallel optical microscope studies (*Figure 2*); these observations are consistent with previous light scattering data for the same PC–PMMA system[4]. In the very early stages of phase separation, where it is difficult to monitor the fine texture of the phases by optical microscopy, we observed increases in intensity of the absorption peak for PC–PMMA at constant wavelength and a new peak develops (with $\lambda_{max} \approx 240$ nm), see *Figure 1*. In the later stages, when the phase structure coarsens, λ_{max} for this new peak shifts to longer wavelengths.

In the case of PS–PVME blends, which have a lower viscosity at the temperature used, we were unable to study the rapid initial development of a new 'absorption' peak but we observed the subsequent shift (and broadening) of a peak to longer wavelength as phase ripening occurred (*Figure 1b*).

Similar changes in the absorption spectra during phase separation were also observed on a Perkin–Elmer Lambda 5 spectrophotometer, demonstrating that the phenomenon is not instrument specific; an advantage of the HP8452 diode-array spectrophotometer is the high speed of spectrum acquisition.

We attribute the observed changes in the absorption spectra to diffraction effects produced by the samples and associated with morphological changes during phase separation. Thin films with phase-separated morphologies can be considered as a kind of diffraction grating in which the interfaces between regions of different refractive index act as diffraction edges.

For a conventional diffraction grating the fundamental equation is:

$$d \sin \theta = m\lambda$$

where d is the distance between lines in the grating, θ is the diffraction angle, λ is the wavelength of the diffracted light and m is the order of diffraction maximum.

In our experiments the diffracted light, which is scattered out of the transmitted beam detected by the spectrophotometer, corresponds in the spectra to 'absorbed' light. Thus, while many workers monitor the intensity and angle of scattered light directly, we have observed the integrated loss of scattered intensity (except for directly forward-scattered light) from the transmitted beam. Also, while most workers use monochromatic radiation, we have, in effect, studied scattering with white light. As in conventional scattering experiments, where larger particles scatter light at longer wavelengths, we observe a loss of transmitted light at longer wavelengths for larger phase-separated structures. Possibly the increasing loss in transmitted intensity at constant λ ($\approx$240 nm), in the early stages of phase separation for the blend PC–PMMA, might be associated with increased scattering by developing structures of constant size, as in spinodal decomposition. Then, as the distance between phase boundaries increases as the phase domains coalesce and the morphology ripens, the peak shifts to larger λ.

We are now studying the kinetics of phase separation in polymer blends in an attempt to quantify the relationship between phase-separated morphologies and corresponding spectra, i.e. we hope to determine any correlation functions which relate λ_{max} and peak widths to phase dimensions and order. We also aim to correlate the observations with low-angle light scattering and small-angle X-ray scattering studies and determine any relevant correlation functions.

To the best of our knowledge, this work represents the first study of phase separation, especially in polymer blends, by u.v.–visible spectroscopy. The observations indicate that the phenomenon is general and not specific to a particular blend system or instrument. We consider that these preliminary observations might form the basis of a fast, simple and effective technique for monitoring phase separation and morphological changes where these processes take place on a time-scale compatible with spectrum determination.

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