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Mutual diffusion in a miscible polymer blend

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Self-diffusion in polymer melts has been extensively studied and is reasonably well understood in terms of the reptation model[1–4]; the related phenomenon of mutual diffusion in miscible blends of chemically different polymers has received little attention, despite its practical relevance and implications for physical processes, such as phase separation kinetics. In such blends, attractive interactions between the monomers, when summed over a polymer chain, may lead to large enthalpic driving forces favouring the mixing; this in turn results in a mutual diffusion rate which is rapid compared with the entropically driven self-diffusion[5], and which is strongly composition-dependent[6]. We have measured mutual diffusion as a function of composition in one such binary blend, polyvinyl chloride (PVC)/polycaprolactone (PCL), and report here that the mutual diffusion coefficient is strongly enhanced in the middle of the composition range. This result is qualitatively, though not quantitatively, in accord with the results of some recent theoretical treatments[5–8].

The molecular characteristics of the polymers used are given in Table 1. Diffusion coefficients were determined by measuring the broadening with time of an initially step-like concentration profile. A sharp interface was set up between blends of PVC and PCL differing in concentration by 10%; the sample was then held at a temperature of 91.5 ± 0.5 °C in a vacuum oven for known times (8 h to 7 days). The final distribution of the two polymer species after diffusion-broadening across the interface was then determined using X-ray microanalysis in a scanning electron microscope, in which X rays from inner-shell transitions excited by the electron beam, and characteristic of the element producing them, are counted by a detector. In this case we measured the concentration of chlorine atoms in the PVC across the sample; the spatial resolution of this technique is 3 μm, and with careful sample preparation a concentration resolution of 1% is possible. The resulting broadened profile was analysed using the standard Fick's law solutions to the diffusion equation, to yield directly the value of $D(c)$, the mutual diffusion coefficient at the average concentration c of the diffusion couple. Examples of concentration profiles before and after broadening are given in Fig. 1. Previous workers have used a similar technique[9,10], but in these earlier studies pure materials were allowed to interdiffuse; this does not give satisfactory information about the concentration dependence of the diffusion coefficient for the polydisperse polymers used in experimental

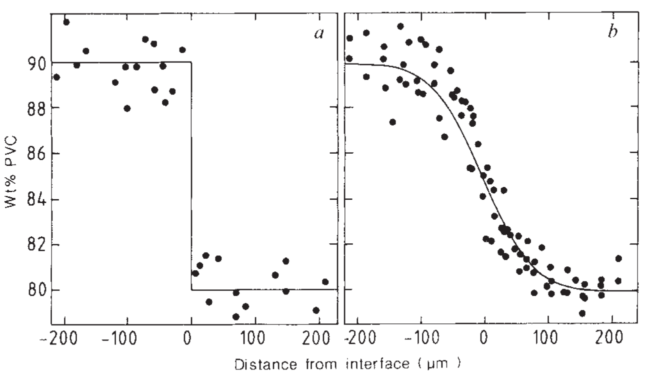

Fig. 1 *a*, Initial concentration profile between two blends (80% PVC/20% PCL, 90% PVC/10% PCL) as revealed by X-ray microanalysis immediately after joining. *b*, Concentration profile after annealing under vacuum for 114.2 h at 91.5 °C. The solid curve is an error-function fit corresponding to $D = 7.42 \times 10^{-11}$ cm^2 s^{-1}, obtained by least-squares analysis. The figure is a composite of five individual profiles measured from different sections of the same diffusion couple. The scatter of each point is ~2–3 times that expected due to counting statistics.

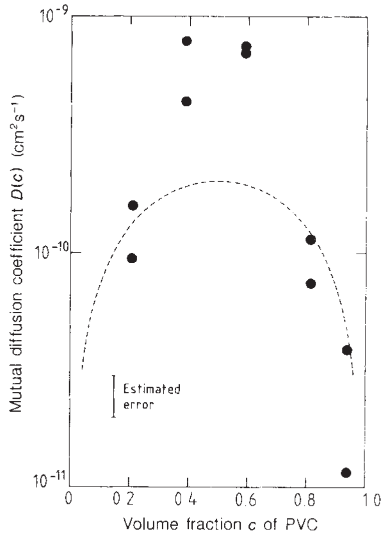

Fig. 2 The measured variation of $D(c)$ with blend composition for the miscible polymer blend PVC/PCL at 91.5 °C. The concentration plotted is the mean volume fraction of PVC in the diffusion couple. Each point corresponds to a value of $D(c)$ taken from a composite concentration profile such as that in Fig. 1, made up of several different profiles for the same diffusion time. Points for a given c correspond to runs carried out over times differing by a factor of ~3. The broken line shows the concentration dependence predicted by equation (1), assuming D_0 to be constant and neglecting the difference in degree of polymerization of the polymers. The actual value chosen for D_0 is arbitrary.

Table 1 Relative molecular masses (M_rs) of polymer samples

Polymer	M_w	M_n	M_w/M_n
PVC	83,500	37,400	2.2
PCL	33,000	10,700	3.1

The polymers used in this study were purchased from Aldrich Chemical Co., and were used as supplied. The M_r characterizations, supplied by Aldrich, were obtained by light scattering and gel-permeation chromatography. M_w, weight-averaged M_r: M_n, number-averaged M_r.

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work, as the standard methods for obtaining this information from diffusion profiles apply only to strictly binary systems[11].

Figure 2 shows the measured variation of $D(c)$ with concentration, based on profiles such as that in Fig. 1. A marked maximum in $D(c)$ towards the centre of the concentration range is apparent.

A prediction for the concentration dependence of $D(c)$ is provided by some recent analyses. As in the case of small molecules, the mutual diffusion coefficient may be written as the product of a mobility term and a thermodynamic term expressing the departure from ideality of mixing[12]. The thermodynamic term may be evaluated using the Flory-Huggins theory for the free energy of mixing of a polymer blend; for polymers of identical chain lengths this gives[6-8]

$$D(c) = D_0[1 - 2\chi Nc(1-c)] \qquad (1)$$

where c is the volume fraction of one polymer, D_0 is a coefficient expressing the mobility of the components (if the two materials have identical mobilities this would correspond to their self-diffusion coefficient), and χ is an interaction parameter (for polymers to be miscible χ must be $<1/2\,N$). For this sytem χ has been estimated by melting-point depression, and is expressed per monomer unit of PCL ($\chi = -0.38$)[13]. The presence of the polymerization index N ensures that the second term in equation (1) dominates for all but the smallest concentrations; that is, the diffusion is driven by enthalpy rather than by entropy. It is this that leads to the characteristic observed concentration dependence. For polymers with differing molecular masses the thermodynamic term is slightly different[8]; this introduces a skewing of the curve towards the region rich in the longer polymer.

The measured concentration dependence in the system we have studied is rather stronger than the simple quadratic relation given in equation (1) (compare with broken line in Fig. 2). Quantitative agreement with this result is not to be expected, because of the simplifications in the model used. In particular, no microscopic theory exists for the average mobility term D_0 when the polymers have different mobilities. In this system it is clear that there are large differences between the mobilities of the pure components; this is reflected in the large variation of glass transition temperature with composition[14]. Nonetheless, the present study shows directly for the first time that in a miscible polymer blend the mutual diffusion coefficient does indeed vary strongly with blend composition; a maximum is indicated near the middle of the blend composition range, in qualitative agreement with recent theoretical treatments.

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Vortex flow visualizations reveal change in upstroke function with flight speed in bats

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The flapping wings of flying birds and bats generate complex, unsteady air movements. These consist of well-defined vortex structures which are a necessary result of the aerofoil action of the wings, and which transport momentum below and behind the animal in reaction to the lift force which both balances weight and provides thrust[1]. Visualization of the vortex patterns enables the aerodynamic function of the flapping wings to be determined[2-6]. Here we present the results of experiments with small vespertilionids which allow the first description of the vortex wake of bats. The aerodynamics of flapping flight is similar between birds and bats: thrust is always generated during the downstroke, but wingbeat gait (the cyclic pattern of wing movements) and the mechanical function of the upstroke are determined by wing morphology. We present the first evidence from aerodynamic experiments that in an individual bat or bat species, upstroke function and wingbeat gait also vary with flight speed, with aerodynamic lift being generated during the upstroke at high speeds but not during slow flight. This result confirms that flapping gaits are not species-specific, but are selected according to the mechanical conditions experienced by the animal.

We trained long-eared bats (*Plecotus auritus* L.) and noctules (*Nyctalus noctula* L.) to fly through a cloud of neutrally buoyant helium-filled soap bubbles, and recorded wake airflows by photographing the movements of the bubbles in stereo; illumination by four electronic flash guns fired successively at short intervals (8-12 ms) enabled vortex-induced air speeds to be determined, since speed is proportional to the distance between bubble images. Discrete vortices are identified by localized high flow velocities and pronounced rotational flows. This method has been applied to various species of birds[3,4,6], but has not been used previously with bats. Figures 1-3 show typical photographs from a total of about 250 of the two species, together with sketches, drawn from stereo pairs, of the associated discrete vortex patterns.

Wake photographs should be interpreted in relation to the balance of forces on the flying animal. The lift on the flapping wings acts horizontally as a thrust as well as vertically supporting the weight. If weight support alone were required the wings would not need to be flapped (a fixed gliding wing can generate sufficient lift to equal weight), but flapping of the wings must serve also to balance frictional and vortex drag forces: in gliding flight drag is uncompensated, and the animal has no alternative but to descend or decelerate relative to the air. The wake vortices transport momentum, the mean reaction of which in flapping flight is experienced as a lift force acting on the wings and providing *both* thrust and weight support. In the downstroke the wings move forwards and downwards relative to the air, and lift has the required forwards and upwards action[1,5,7,8]. In the upstroke, however, the wings move primarily upwards; at high flight speeds they also travel forwards, the air flow meets the ventral side of the wing as in the downstroke, and if lift is to contribute to weight support it cannot also give thrust, but must retard the animal[5-7]. In slow flight the wings may move slightly backwards relative to the air; lift forces are likely to be small or absent[1,7], but it has been suggested that if in bats the air flow strikes the dorsal surface of the wing, the resulting weak lift may act as both thrust and weight support[5,7,8].

Thus, upstroke function is the main mechanism of differentiation between flapping flight gaits in flying vertebrates, and the upstroke may be expected to act in different ways at different flight speeds. Experiments with birds have confirmed that gaits are constrained by wing morphology[2-6]: an active, lifting