

Variation in optical density during latex film formation: interdiffusion of fluorescence labelled polymers

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Steady state fluorescence was used to examine the interdiffusion of polymer molecules during annealing of a latex film at and above the glass transition temperature. The film was prepared from a mixture of poly(methyl methacrylate) latex particles labelled with naphthalene (donor) and pyrene (acceptor). It was observed that the optical density (index of refraction) of the latex film changed considerably during the annealing process. Donor and acceptor intensities were required to compensate for this effect. The activation energy for polymer chain interdiffusion was found to be 34 kcal mol⁻¹.

(Keywords: fluorescence; interdiffusion; latex film; optical density)

Introduction

When a latex dispersion is dried by evaporation of solvent from its surface, the polymer particles are driven closer together until the stabilizing forces are overcome. The latex then forms a continuous film by coalescence of the polymer particles. There are three stages in the formation of the latex film. During the first stage, as solvent evaporates the solid concentration increases until the particles become closely packed. In the intermediate stage, the particles deform under the forces generated by evaporation of solvent, filling the interstitial spaces between particles. This process occurs only at temperatures above the minimum film-forming temperature (MFT) which often lies close to the glass transition (T_g) of the latex polymer. In the final stage, interdiffusion of polymer chains between adjacent particles causes further coalescence.

In the last few years, the process of interparticle polymer diffusion has been studied by direct non-radiative energy transfer (DET) using a fluorescence decay method with particles labelled with donor and acceptor dyes¹⁻³. This method has been employed to study film formation of poly(methyl methacrylate) (PMMA) particles 1 μ m in diameter and poly(butyl-methacrylate) (PBMA) particles 100 nm in diameter^{2,3}. In each of these studies it was found that annealing leads to polymer diffusion as the particle interface heals.

In this work the third stage of particle coalescence was studied using DET, as measured using steady state fluorescence. The PMMA particles were prepared by non-aqueous dispersion (NAD) polymerization. These particles were labelled with appropriate donor (naphthalene) and acceptor (pyrene) chromophores^{4,5}.

The particles used (1–3 μ m diameter) have two components. The major part, PMMA, comprises 96 mol% of the total monomer content of the material. The minor component, polyisobutylene (PIB, 4 mol% monomer), forms an interpenetrating network through the particle interior^{6,7}, very soluble in certain hydrocarbon

media. A thin layer of PIB covers the particle surface and provides colloidal stability by steric stabilization.

Latex films were annealed for 1 h at various temperatures at and above the T_g of PMMA. We observed that during the transparent film formation the optical density of the coalescing latex changed considerably. In such studies this is very important, since the variation in optical density of the latex film complicates the determination of the extent of DET. However, in this work the donor and acceptor intensities were corrected to compensate for this effect such that the DET phenomenon could be isolated and used to detect and study the interdiffusion of polymer chains during latex film formation. Increase in the extent of DET (measured at a fixed time following film 'casting') with temperature was treated by a classical diffusion treatment and the activation energy of polymer chain interdiffusion was calculated.

Experimental

Naphthalene (N) and pyrene (P) labelled PMMA-PIB polymer particles were prepared by NAD polymerization. Details of preparation have been reported elsewhere⁵. A stable spherical dispersion of polymer particles was used, ranging in diameter from 1 to 3 μ m. A combination of ¹H n.m.r. and u.v. analysis indicated that these particles contained 6 mol% PIB, 0.37 mmol N and 0.037 mmol P groups per gram of polymer.

Latex film was prepared by dispersing the same mass of N and P particles in heptane in a test tube. After complete mixing, a large drop of the dispersion was placed on a round silica window plate with a diameter of 2 cm. Heptane was allowed to evaporate and the silica window was placed into the solid surface accessory of a fluorescence spectrometer (Perkin-Elmer, model LS-50). Slit widths were kept at 2.5 nm. For DET experiments the N-P film sample was excited at 286 nm in order to maximize naphthalene absorbance while minimizing pyrene absorbance.

The film of latex particles was annealed at and above the T_g of PMMA for 1 h at various temperatures. The temperature was maintained within $\pm 2^\circ\text{C}$ at each step

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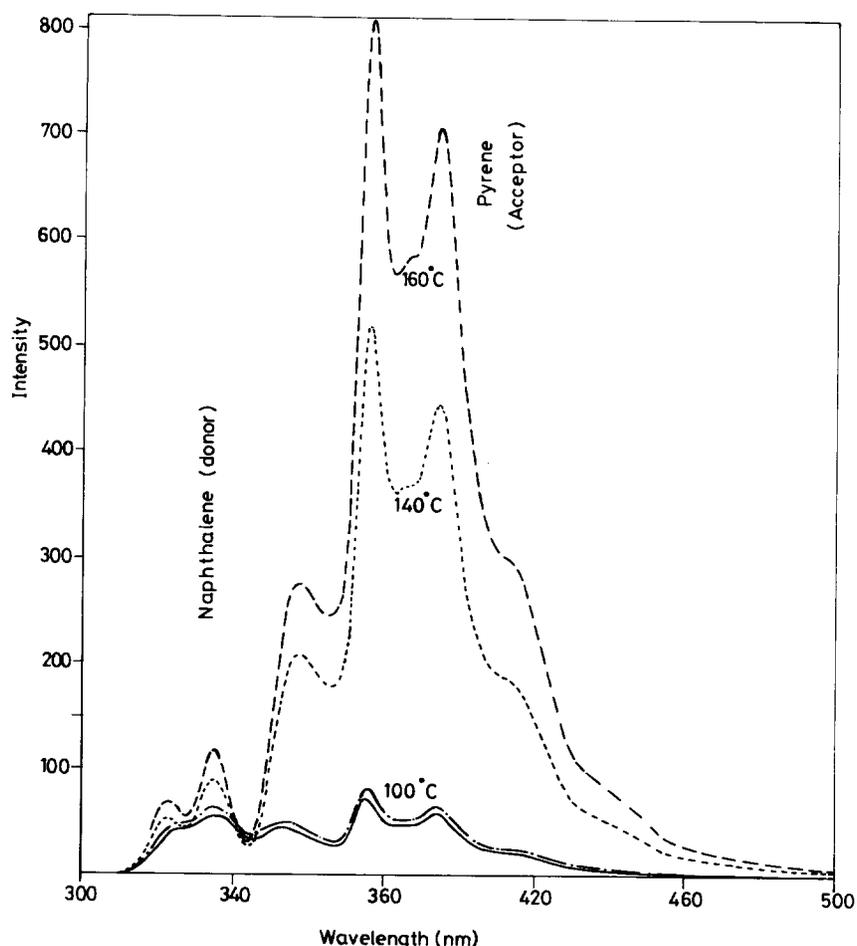


Figure 1 Emission spectra of N-P latex film annealed for 1 h at 100, 140 and 160°C. Samples are excited at 286 nm. The solid line indicates the spectra before the annealing process started

of the annealing process. All measurements were carried out in the front face geometry at room temperature.

The variation in optical density of N-P film was controlled by only exciting pyrene at 345 nm for each measurement. Emission intensity of pyrene was taken as a standard for the correction in the intensities of DET experiments.

Results and discussion

The emission spectra of N-P latex film annealed at 100, 140 and 160°C are presented in Figure 1. Below 120°C no change was observed in the donor, $I_N(T)$, and acceptor, $I_p(T)$, intensities; however, above 120°C both intensities increased continuously, then decreased with increasing annealing temperature. From the point of view of DET the increase in $I_p(T)$ is understandable; however, the increase in $I_N(T)$ is quite surprising. A decrease in $I_N(T)$ would be expected due to DET processes as $I_p(T)$ is increased. In order to solve this contradiction, the result of a control experiment was used where pyrene was excited directly at 345 nm in N-P latex film. In this case the temperature variation in pyrene emission intensity $I_{op}(T)$ showed similar behaviour to $I_N(T)$ and $I_p(T)$. Since pyrene was excited at 345 nm, variation in $I_{op}(T)$ must be related only to changes in optical density of the latex film during the annealing processes above 120°C. Latex film probably became more transparent as the annealing temperature increased; more light could pass through and excited more molecules. As a result,

the emission intensity of pyrene increased as the temperature increased. $I_{op}(T)$ reached a maximum at 180°C, which is presumably the healing temperature of the latex film. At this temperature, interfaces between particles disappeared and the film became completely transparent. Above 180°C the decrease in $I_{op}(T)$ can be related to the decrease in thickness of the latex film as the temperature increased.

Corrections must be made to $I_N(T)$ and $I_p(T)$ intensities to isolate the DET phenomenon, which may help us to understand the interdiffusion of the polymer chains. Since all the experimental conditions are the same, emission intensity, $I_{op}(T)$, of pyrene is taken as a standard for each experiment, then $K(T) = I_{op}(T)/I_{op}(0)$ can be used as a correction factor for $I_N(T)$ and $I_p(T)$ intensities. The corrected donor and acceptor intensities were found to be $I_{KN}(T) = I_N(T)/K(T)$ and $I_{Kp}(T) = I_p(T)/K(T)$, respectively, and were plotted versus annealing temperature, as shown in Figures 2a and b. It can be seen that the acceptor intensity $I_{Kp}(T)$ increased as donor intensity $I_{KN}(T)$ decreased due to energy transfer from excited naphthalene to ground state pyrene.

The interdiffusion process can be quantitatively interpreted by using a classical diffusion model⁹, developed by Tirrell *et al.*⁸. These researchers studied chain diffusion across a planar interface in terms of acceptor emission intensity due to energy transfer. When a donor molecule is excited, it transfers its energy to nearby acceptor molecules, then the fluorescence

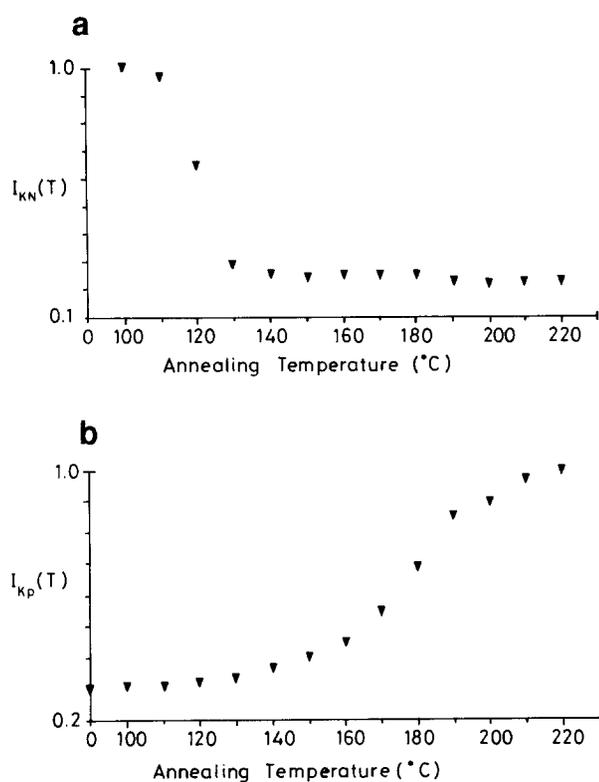


Figure 2 Corrected donor and acceptor emission intensities versus annealing temperature in N-P latex film [$K(T) = I_{op}(T)/I_{op}(0)$ is the correction factor]. (a) donor: $I_{KN}(T) = I_N(T)/K(T)$; (b) acceptor: $I_{KP}(T) = I_p(T)/K(T)$. Intensities are normalized to unity

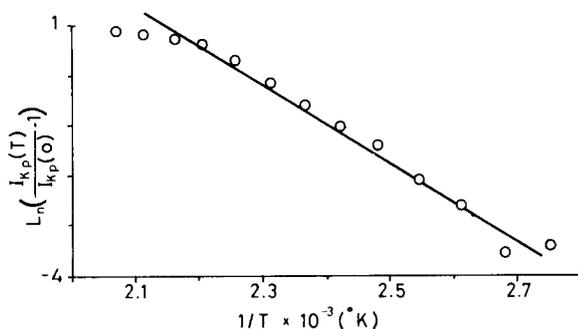


Figure 3 Arrhenius plot of equation (3)

intensity of acceptor increases with time according to the relation⁸:

$$I(t) - I(0) = I_0 0.165 \alpha C_0^2 \sqrt{Dt} \quad (1)$$

Here $I(0)$ is the fluorescence intensity at time zero before any interdiffusion has taken place, I_0 is the incident light intensity, α is the proportionality constant which can be determined experimentally and C_0 is the interface concentration of acceptor molecules. Here the assumption is made that diffusion time is long compared to the longest configurational relaxation time of the polymer chain.

In equation (1), the centre of mass diffusion coefficient, $D(T)$, of polymer chains obeys the Arrhenius relation according to:

$$D = D_0 e^{-\Delta E/kT} \quad (2)$$

where ΔE is the activation energy for the interdiffusing chains and k is the Boltzmann constant. Substituting equation (2) in equation (1) a useful relation is obtained to interpret the temperature variation of the corrected acceptor intensity in Figure 2b. For a fixed time (1 h) this relation is written as:

$$\left[\frac{I_{KP}(T)}{I_{KP}(0)} - 1 \right] = R e^{-\Delta E/2kT} \quad (3)$$

where R is the coefficient for the related constants in equations (1) and (2). The logarithmic plot of equation (3) gives a good linear relation (see Figure 3) with an activation energy of 34 kcal mol^{-1} . Previously¹, using the time-resolved fluorescence method, a similar activation energy (37 kcal mol^{-1}) was measured for PMMA latex particles during film formation above T_g . With the same method, Winnik *et al.*^{2,3,10} found apparent activation energies of 38, 38.9 and 34 kcal mol^{-1} for PBMA latex particles during annealing at and above T_g . In the 1950s, based on creep compliance measurements, Ferry and co-workers suggested that these activation energies are characteristics of PBMA chain backbone motion^{11,12}. Using fracture techniques, with time to fracture less than 10^{-6} s , a lower limit for the activation energy of the backbone was reported as 40 kcal mol^{-1} for bulk PMMA¹³.

In Figure 3 one can see that 120°C is the onset temperature at which chain diffusion starts. Above 120°C the variation in optical density [$I_{op}(T)$] proceeds parallel to the interdiffusion of polymer chains during the annealing processes. As polymer chains diffuse across the boundary of the particles, interfaces heal and eventually disappear. At 180°C , interdiffusion eventually gives the latex film a transparent, homogeneous structure. Interdiffusion of polymer chains saturates above 220°C where PMMA melts.

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