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Healing and interdiffusion processes at particle–particle junction during film formation from high-T latex particles

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When amorphous polymers of same type are brought into contact at temperatures above the glass transition, the interface gradually heals and junction boundaries eventually disappear. Here we used a steady-state fluorescence technique to examine the healing and interdiffusion of polymer molecules during annealing of latex film above the glass transition. The film was prepared from a mixture of naphthalene- (donor) and pyrene- (acceptor) labelled poly(methyl methacrylate) latex particles. We report that during the annealing processes the transparency of the film changed considerably. Healing temperature (T_H) and time (τ_H) were measured when the latex film became almost transparent. Above T_H interdiffusion of polymer chains was observed by detecting the energy transfer from excited naphthalene to pyrene molecules. Healing and diffusion activation energies were calculated and found to be 9.84 kcal mol^{-1} and 30 kcal mol^{-1}, respectively, for the annealed latex film samples.

(Keywords: interdiffusion; particle–particle junction; high-T latex)

INTRODUCTION

When two identical polymers are brought into contact at a temperature above their glass transition temperature, the junction surface gradually disappears and becomes indistinguishable from any other surface that might be located within the bulk material. Brownian motion drives the polymer chains across the junction until eventually all traces of the original interface are lost; at this point was say the junction has 'healed'. Many years ago Vayutskii[1] suggested that the formation of a continuous, strong and water-impermeable film involves polymer diffusion across the junction of identical polymer particles. The molecular interpenetration of the healing process is related to the phenomenon of self-diffusion in bulk polymers, but the two are not identical. In self-diffusion, polymer coils move over distances many times their mean diameter, whereas healing is eventually complete in the time it takes a polymer coil initially next to the junction surface to move halfway across it. The 'healing time' (τ_H) can then be comparable to the configurational relaxation time (τ_e) of a polymer chain. When polymer chains are much longer than a certain length, diffusion of chains is pictured as a worm-like motion described by the reptation model, proposed by de Gennes[2]. The reptation time (T_r) gives the time necessary for a polymer to diffuse a sufficient distance for all memory of the initial tube to be lost. Prager and Tirrell[3] derived a relation for the crossing density of the chains by using the reptation model during the healing process. Wool and O'Connor[4] employed reptation to study crack healing in terms of several stages, including wetting, diffusion and randomization, where at the end of the wetting stage, potential barriers associated with the inhomogeneities at the interface disappear and chains are free to move across the interface by a randomization process.

Latex films are traditionally formed from two categories of dispersions. The first category comprises aqueous dispersions of colloid particles with T_g below the drying temperature, known as low-T latex (soft latex)[5–7] dispersions in which the particles are of submicrometre size. The second category includes acqueous and non-aqueous dispersions of colloidal particles where T_g exceeds the drying temperature, called high-T latex (hard latex)[8] dispersions, where the diameters of the spherical particles ranged from 0.1 to 10 μm. High-T and low-T latex dispersions can be distinguished by the nature of their inherited coalescence. High-T latex particles remain essentiallly discrete and undeformed during drying, such that coalescence occurs subsequently at higher temperatures, driven by healing and interdiffusion processes. By contrast, coalescence of the low-T latex particles occurs during drying and the process is strongly dependent on colloidal interactions in the dispersion, stabilizing surfactants and the drying process itself. In the latter case particles are deformed to polyhedrons after solvent evaporation where the deformation is driven by a combination of surface and osmotic forces.

Transmission electron microscopy (TEM) has been used to examine the morphology of dried latex films[9,10]. These studies have shown that in some instances the

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particle boundaries disappeared over time, but in other cases the boundaries persisted for months. It was suggested that in the former case particle boundaries healed by polymer diffusion across the junction. In the last few years, it has become possible to study latex film formation at the molecular level. Small-angle neutron scattering (SANS) was used to examine deuterated particles in a protonated matrix. It was observed that the radius of the deuterated particle increased in time as the film was annealed[11] and as the polymer molecules diffused out of the space to which they were originally confined. The process of interparticle polymer diffusion has also been studied by the direct energy transfer (DET) method, using transient fluorescence measurements[5,8,12,13] in conjunction with latex particles labelled with donor and acceptor chromophores. These studies all indicate that annealing leads to polymer diffusion and mixing as the particle junction heals during latex film formation.

In this paper continuous film formation from high-T latex (poly(methyl methacrylate) (PMMA)) particles was studied after solvent evaporation. PMMA particles, labelled with naphthalene (N) donor and pyrene (P) acceptor were prepared by non-aqueous dispersion (NAD) polymerization. The particles of diameter 1–3 μm used had two components; the major part, PMMA, comprised 96 mol% of the material and the minor component, polyisobutylene (PIB) (4 mol%), formed an interpenetrating network through the particle interior, very soluble in certain hydrocarbon media. A thin layer of PIB covered the particle surface and provided colloidal stability by steric stabilization.

Various stages of particle coalescence were generated by annealing the dried latex films at equal time intervals above the glass transition temperature (T_g) of PMMA. Pyrene fluorescence intensities were measured by the steady-state technique. Variation in P intensities with respect to annealing temperature were used to study the healing process at particle–particle junctions. Healing times (τ_H) at elevated temperatures were measured and the activation energy for the randomized polymer chain segments across the junction was found. Above τ_H, the increase in pyrene intensity due to energy transfer from N to P at elevated annealing temperatures was explained by the interdiffusion of polymer chains. An activation energy for the diffusing polymer chain was found that was three times larger than the healing activation energy. This was attributed to the backbone motion of the chain.

EXPERIMENTAL

Naphthalene (N)- and pyrene (P)-labelled PMMA–PIB polymer particles were prepared separately in a two-step process in which in the first step methyl methacrylate (MMA) was polymerized to low conversion in cyclohexane in the presence of PIB containing 2% isoprene units to promote grafting. The graft copolymer so produced served as a dispersant in the second stage of polymerization, in which MMA was polymerized in a cyclohexane solution of the copolymer. Details have been reported elsewhere[14–16]. A stable spherical dispersion of polymer particles was produced, ranging in radius from 1 to 3 μm. A combination of ^{1}H-n.m.r. and u.v. analysis indicated that these particles contain 6 mol% PIB and 0.37 mmol N and 0.037 mmol P groups per gram of polymer.

Latex film preparations were carried out in the following manner. The same weights of N- and P-labelled particles were dispersed in heptane in a test-tube; after complete mixing, a large drop of the dispersion was dropped on a round silica window plate with diameter of 2 cm. Heptane was allowed to evaporate and the silica window was placed in the Solid Surface Accessory of a Perkin–Elmer Model LS-50 fluorescence spectrometer. All measurements were carried out in the front face position at room temperature. Slit widths were kept at 2.5 mm. Film thicknesses were measured by weighing the silica plate before and after the film casting and estimated to be around 2–3 μm.

In this work two separate fluorescence experiments were performed. In the first set of experiments, after evaporation of heptane, N–P film was annealed above the glass transition temperature of PMMA in equal time intervals at elevated temperatures between 110 and 220°C. Only P was excited when 345 nm fluorescence emission spectra were measured at room temperature. In the second set, DET experiments were performed with the same N–P sample described above by exciting N and detecting the full fluorescence spectra of N and P. Here the N–P film sample was excited at 286 nm in order to maximize naphthalene absorbance while minimizing pyrene absorbance. Film samples were illuminated only during the actual fluorescence measurements and were shielded from the light source at all other times. The temperature was maintained within ± 2°C during the annealing. Emission intensities of P in the first set were taken as a standard for the correction on the N and P intensities in the DET experiments. In all experiments maximum peak heights at 334 nm and 375 nm were used for N and P intensities, respectively. Peak ratios were always checked in the N–P spectra during the experiments.

RESULTS AND DISCUSSION

Healing at the particle–particle junction

The emission spectra of the N–P latex film when excited at 345 nm and annealed at elevated temperatures for 180 min intervals are shown in *Figure 1*. P intensity was first increased and reached a maximum at 130°C, then decreased on increasing the temperature. This behaviour of the P intensity for other N–P film samples was repeated upon annealing at other time intervals, except that the maximum in the P intensity shifted to higher temperatures for smaller annealing intervals. In *Figure 2* these experimental results are summarized where P intensity, $I_{OP}(T)$, is normalized to unity for each set of experiments for comparison. When the N–P films were annealed in 90, 120, 150 and 180 min intervals, the maximum in P intensity appeared at 130°C. However, as the time intervals for annealing were decreased to 40, 30, 15, 10 and 5 min the temperature for the maximum in P intensity increased to 140, 140, 160, 180 and 210°C, respectively. These results are summarized in *Figure 3*.

The maxima in $I_{OP}(T)$ in each experimental set can be explained by the healing process at the particle–particle junction where polymer chain segments attempt to randomize themselves across the junction surface. The maxima in *Figure 2* might correspond to the 'healing time' (τ_H) for a given temperature, or 'healing temperature' (T_H)

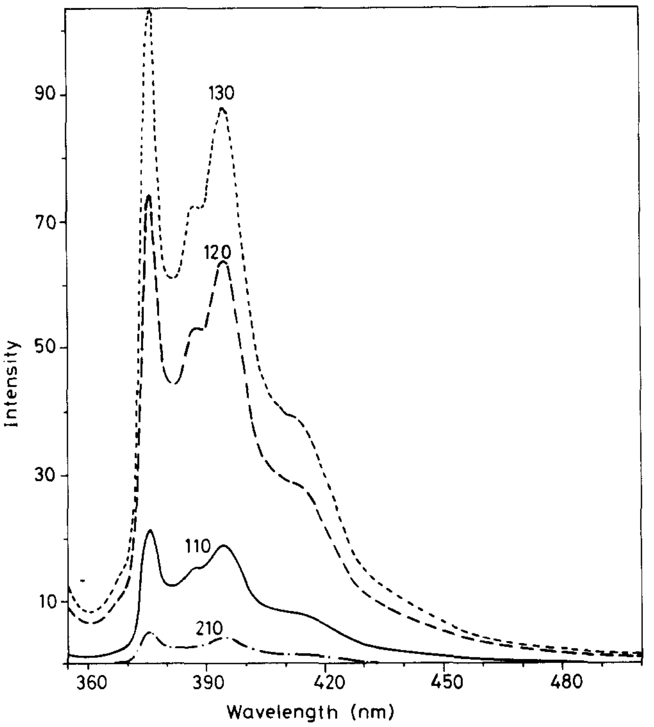

Figure 1 Emission spectra of pyrene (P) when N–P film is excited at 345 nm, after annealing at 110, 120, 130, 190 and 210°C for 180 min intervals

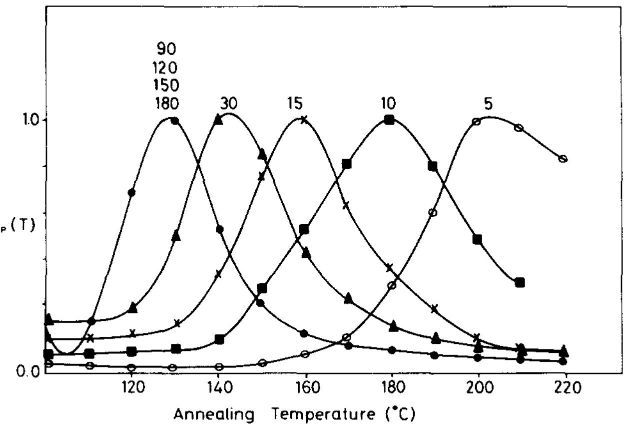

Figure 2 Normalized P intensity, $I_{OP}(T)$ is plotted *vs* annealing temperature. The values above each experimental set represent the annealing time intervals in minutes, N–P samples are excited at 345 nm

for a given time at which the polymer chain presumably moves halfway across the junction surface[3]. For instance, at 140, 160 and 180°C, τ_H values were found to be 30, 15 and 10 min, respectively. At 130°C the same maxima in $I_{OP}(T)$ for the corresponding time intervals may indicate that healing times do not change upon increasing time intervals at this temperature. In other words 130°C is the minimum required temperature for the healing of latex particles during film formation. For a given τ_H and T_H, particle boundaries start to disappear during coalescence and consequently the latex film becomes almost transparent to the exciting light for the pyrene molecule; as a result the emission intensity of P reaches a maximum. Initially, below T_H, due to the sharp particle boundaries or voids between particles, exciting light scatters from the film surface or passes through the film without exciting P molecules. Increasing of temperature causes wetting and initiates segmental motion and as a result polymer chain segments move across the interface. Subsequently, more exciting light can enter the latex film and the emission intensity of P increases. Above T_H, however, a decrease in $I_{OP}(T)$ can be explained by the decrease in the thickness of the transparent latex film, where the energy transfer between N and P becomes important (see next section) due to interdiffusing of polymer chains. In order to confirm the results above T_H, films of various thicknesses were prepared and I_{OP} intensities were measured and plotted against thickness below, at and above T_H[17]. Because of scattering, below T_H, I_{OP} saturated above a certain thickness; however, linear relationships were observed at and above T_H, with a larger slope measured at the lower temperature. Here linear plots give evidence of transparency where in both cases I_{OP} increased proportionally to film thickness[17]. Smaller slopes above T_H explain the behaviour of the thinner films.

In order to quantify the above results we employed the minor chain model developed by Wool *et al.*[18,19]. They used the reptation model of chain dynamics[2] where by a wriggling motion, a chain on average moves coherently back and forth along the centre line of the tube. The portions of a chain that are no longer in the initial tube increase with time and are referred to as a minor chain of length $l(t)$. The conformations of the minor chains are always Gaussian. Kim and Wool[18] derived the average of the $l(t)$ values for times shorter than the tube renewal time (T_r) and found that

$$\langle l^2 \rangle = 2D\tau_H \qquad (1)$$

Here, the curvilinear diffusion coefficient, D, can be in the following form at T_H

$$D = D_\circ \exp(-\Delta E_H / kT_H) \qquad (2)$$

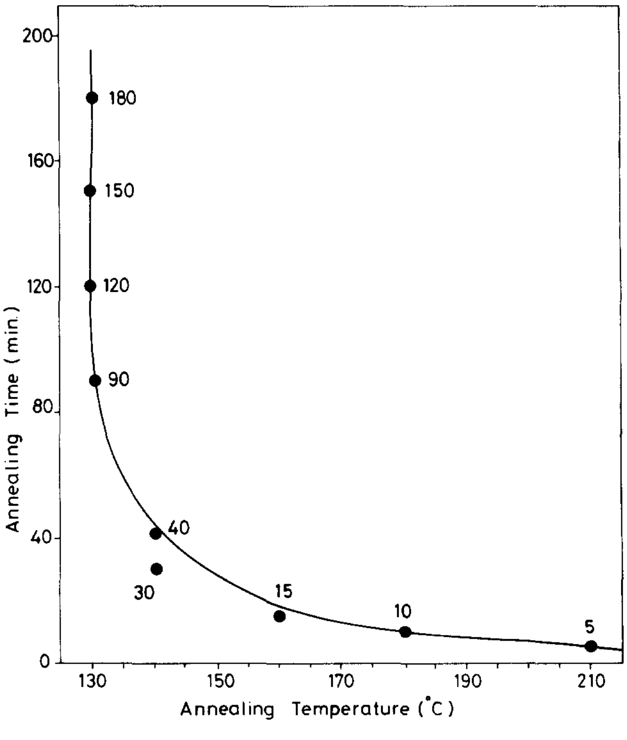

Figure 3 Plot of annealing temperatures *vs* time at maximum $I_{OP}(T)$ intensities of *Figure 2*

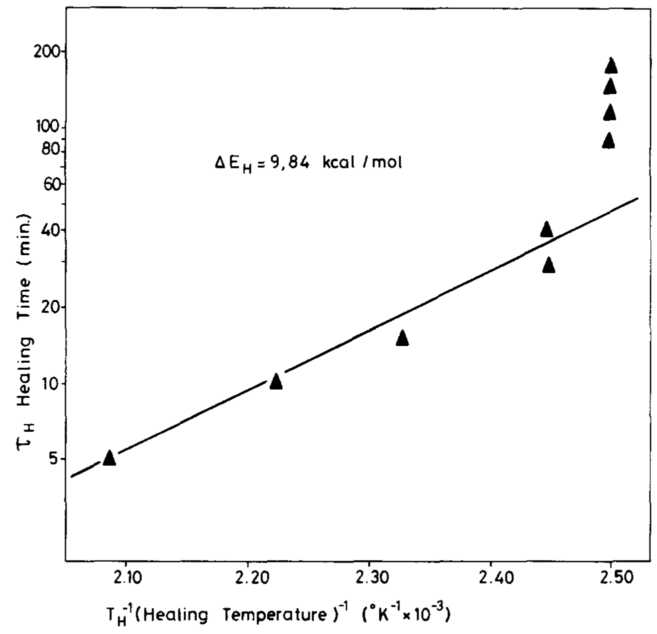

Figure 4 Arrhenius plot of equation (3). ΔE_H is the healing activation energy

where ΔE_H is the healing activation energy, which is the minimum energy required for a minor chain to move across to the junction surface and k is the Boltzman constant. If one assumes that $\langle l^2 \rangle$ values are identical at the healing temperatures of each separate set of experiments, then a very useful relation can be obtained from equations (1) and (2):

$$\tau_H = B \exp(\Delta E_H / kT_H) \qquad (3)$$

where $B = 2D_0 / \langle l^2 \rangle$ is a constant for all sets of experiments in *Figure 2*. Equation (3) is plotted in *Figure 4* and $\Delta E_H = 9.84\,\text{kcal mol}^{-1}$ is obtained from the slope of the linear relation. The activation energy determined in this temperature range is much smaller than for the backbone motion (30–40 kcal mol^{-1})[8] but very close to that typically observed for side-chain motion (9.3 kcal mol^{-1} (ref. 20) and 9.7 kcal mol^{-1} (ref. 21)) for PMMA. After complete wetting it is not unreasonable to accept that the energy requirement for a minor chain to cross the junction surface is much less than the diffusion energy of a backbone in a bulk polymer.

Interdiffusion of polymer chains

In order to study the further coalescence phenomenon in detail, N–P latex film samples were excited at 286 nm after annealing at elevated temperatures in equal time intervals. The emission spectra of N_0–P_0 films annealed at 120, 150, 160 and 210°C for 180 min intervals are shown in *Figure 5*. The variation in N and P emission intensities ($I_N(T)$ and $I_P(T)$), both showed a decrease above healing temperatures, T_H, by increasing annealing temperatures. From the point of view of DET these behaviours of emission intensities look quite strange. When N is excited at 286 nm in N–P film, DET requires a relation

$$N^* + P \rightarrow N + P^* \qquad (4)$$

which suggest that $I_P(T)$ has to increase as $I_N(T)$ decreases by increasing the amount of interdiffusion of N- and P-labelled polymer chains. In order to isolate the DET phenomenon, $K = I_{OP}(T)/I_{OP}(0)$ can be used as a correction factor for the $I_N(T)$ and $I_P(T)$ intensities[20,21], where $I_{OP}(0)$ corresponds to the P intensity at 100°C annealing temperature. Here we assumed that changes in $I_{OP}(T)$ actually related to the variation in 'optical density' of the latex film during the annealing processes[23]. The corrected N and P intensities were obtained as $I_{KN} = I_N(T)/K$ and $I_{KP} = I_P(T)/K$ and are plotted for 90, 30 and 15 min time intervals in conjunction with $I_{OP}(T)$ *versus* annealing temperature in *Figures 6a*, *b* and *c*, respectively. (These corrections are thickness dependent but always work, especially for monolayer latex films[24].) This picture is now more meaningful from the point of view of DET modelling where $I_{KP}(T)$ increases as $I_{KN}(T)$ decreases, above the healing temperature for the N–P latex film samples. Similar behaviours were observed for the other experiments. It is important to note that T_H shifted to a higher temperature region as the annealing time intervals were decreased. From these results it was shown that interdiffusion of polymer chains is activated at temperatures above the T_H. Below T_H, however, an increase in $I_{KN}(T)$ at elevated temperatures can be explained by the disappearance of voids between particles.

When the voids and cracks are present, most of the exciting light may be scattered or pass through the film without exciting N molecules. As the temperature is increased the voids decrease, particles reach complete wetting and more N molecules can be excited. At T_H, since junctions are healed, the film becomes almost transparent and most of the donor molecules are excited and $I_{KN}(T)$ reaches its maximum. Here, the healing temperature (T_H) is, in fact, the onset temperature for the interdiffusion of polymer chains. At temperatures above T_H, acceptor intensity ($I_{KP}(T)$) increased as donor intensity

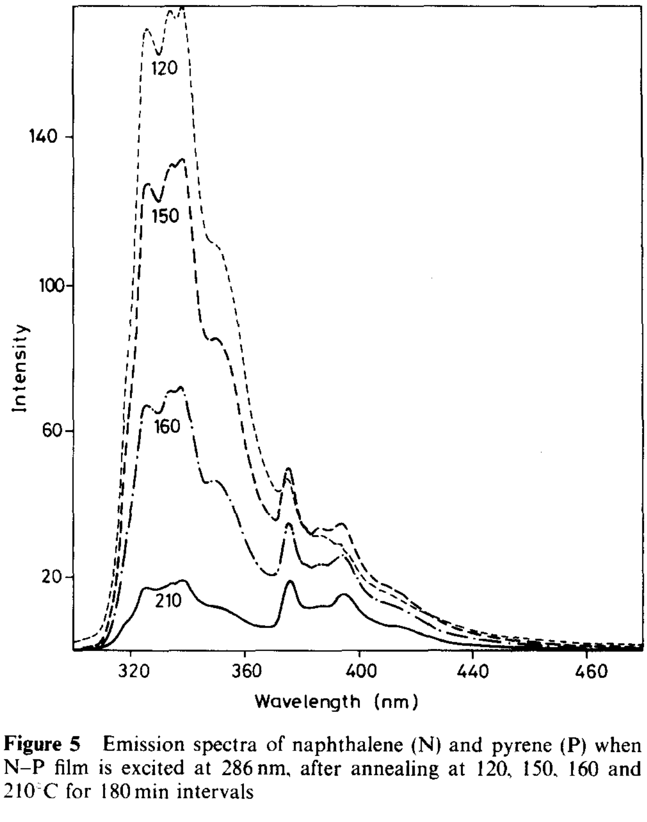

Figure 5 Emission spectra of naphthalene (N) and pyrene (P) when N–P film is excited at 286 nm, after annealing at 120, 150, 160 and 210°C for 180 min intervals

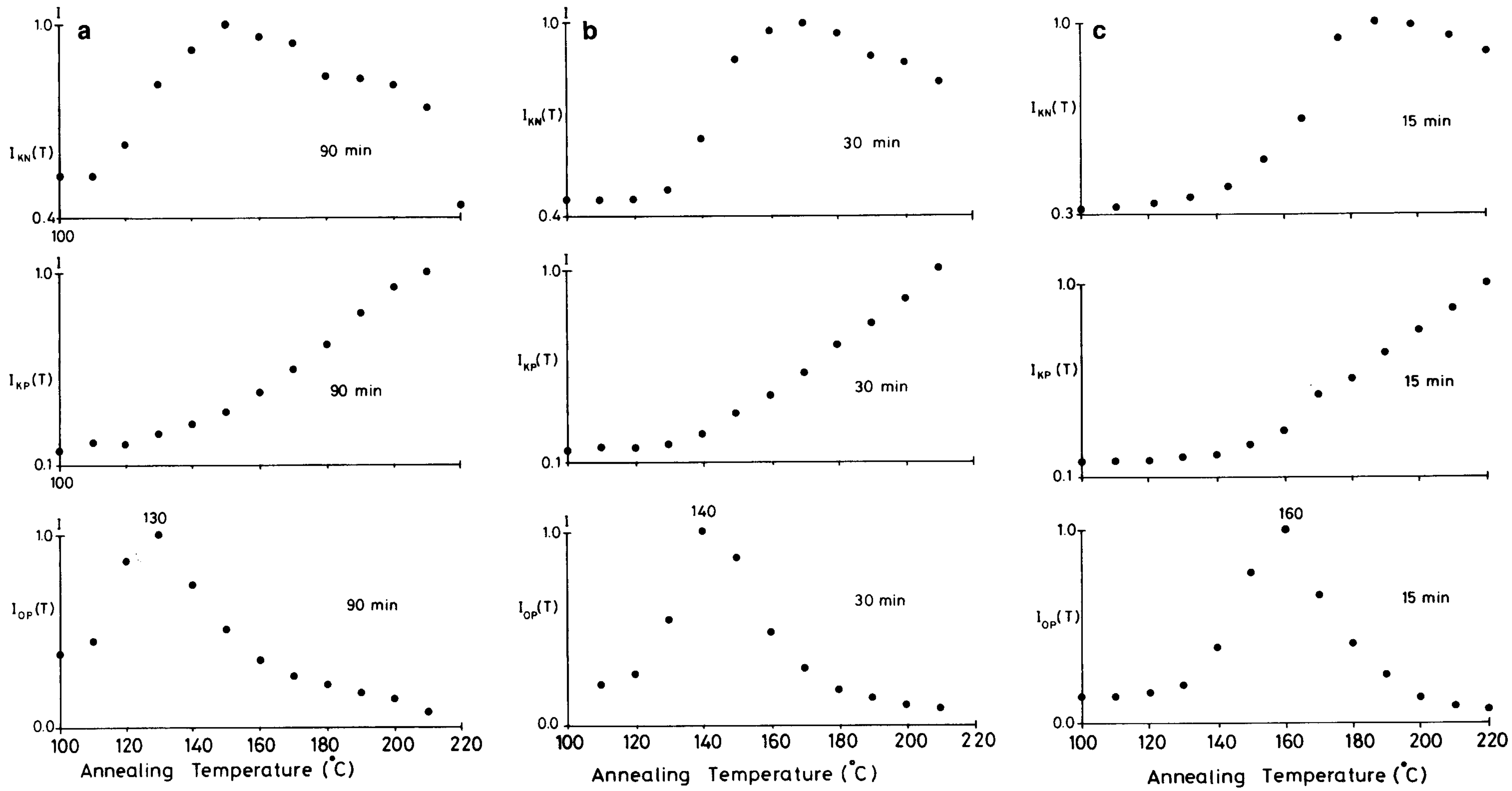

Figure 6 Corrected N and P intensities (I_{KN} and I_{KP}) of samples annealed at elevated temperatures for time intervals of (a) 90 min, (b) 30 min and (c) 15 min. All samples are excited at 286 nm. $I_{OP}(T)$ intensities are given for comparison, where the healing temperatures are indicated by the corresponding values

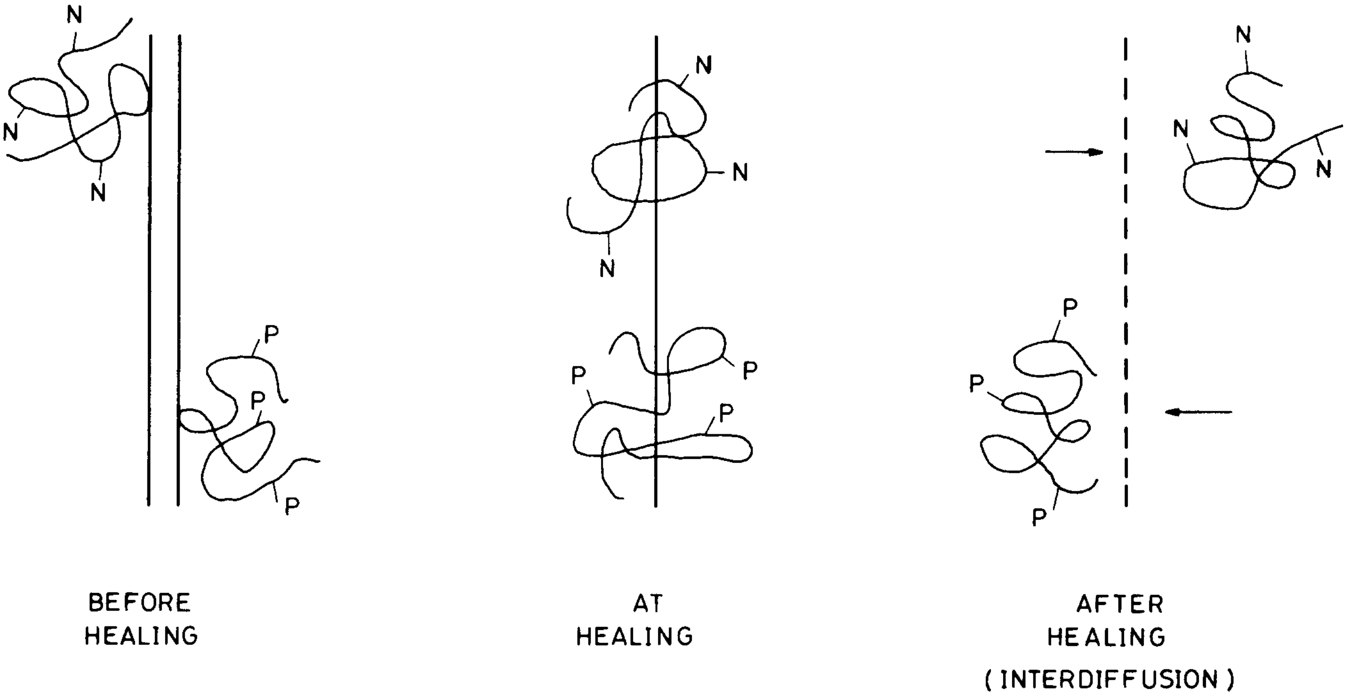

Figure 7 Schematic representation of coalescence phenomena; before healing P and N labelled chains are at the particle–particle junction. At healing, chains cross the junction surface half way. After healing, interdiffusion of polymer chains occurs

($I_{KN}(T)$) decreased, implying that DET takes place as polymer chains start to interdiffuse.

Latex film formation from high-T latex particles can be divided into two main sequential steps: solvent evaporation to the point where the particles begin to touch, and coalescence of the continuous film. Here we studied the coalescence phenomenon in more detail. In the first step, particle–particle boundaries disappear by healing processes and in the second step, which we call further coalescence, chains interdiffuse among each other. The whole picture of healing and interdiffusion is summarized in *Figure 7*. The interdiffusion process can be quantitatively interpreted by using the diffusion model developed by Tirrell *et al.*[25]. They studied the problem in terms of steady-state fluorescence emission intensity of an acceptor due to DET from a donor. This type of experiment was pioneered by Morawetz[26]. Usually when the donor is excited exclusively and can transfer its energy to nearby acceptor groups, the fluorescence intensity of the acceptor will increase with time, thus:

$$I(t) - I(0) = I_0 \alpha \int_{-\infty}^{+\infty} C(x,t)[C_0 - C(x,t)]\,\mathrm{d}x \qquad (5)$$

Here the x-axis is normal to the interface. In equation (5), $I(0)$ is the fluorescence intensity at time zero before any interdiffusion has occurred, I_0 is the incident intensity and α is the proportionality constant, which can be determined experimentally. $C(x,t)$ is the concentration profile of the acceptor at time t. C_0 is the interface concentration. At times long compared with the longest configurational relaxation time (τ_e) of the polymer chain, the concentration profile can be obtained from the classical Fickian diffusion[27]

$$\frac{\partial C(x,t)}{\partial t} = D\frac{\partial^2 C(x,t)}{\partial x^2} \qquad (6)$$

where D is the centre of mass diffusion coefficient of the polymer chain. Here it is important to note that the molecular weight of polymer molecules in the latex particles is small enough to exclude the reptation diffusion model to interpret our DET measurement. During interdiffusion of the polymer chain, we deal with times longer than the healing time τ_H (τ_e), for a given temperature, so the assumption made in order to use equation (6) is quite reasonable.

The solution of equation (6), subject to

$$\begin{aligned} &C(x,0) = C_0 && \text{for } x<0 \\ &C(x,0) = 0 && \text{for } x>0 \\ &C(-\infty,t) = C_0 && \\ &C(\infty,t) = 0 && \text{for all } t>\tau_e \end{aligned} \qquad (7)$$

is

$$C(x,t) = \frac{C_0}{2}(1 - \mathrm{erf}(x/(4Dt)^{1/2})) \qquad (8)$$

Inserting equation (8) into equation (5) and performing the integration:

$$I(t) - I(0) = 0.165 I_0 \alpha C_0^2 (Dt)^{1/2} \qquad (9)$$

can be obtained. In equation (9), the centre of mass diffusion coefficient of the polymer chain obeys the Arrhenius relation as

$$D = D_0 \exp(-\Delta E_P/kT) \qquad (10)$$

where ΔE_P now represents the activation energy for the interdiffusing chain, k is the Boltzmann constant and T is the annealing temperature. Substituting equation (10) into equation (9) one can obtain a useful relation to interpret the temperature variation of corrected acceptor intensities. Since film samples were annealed for equal

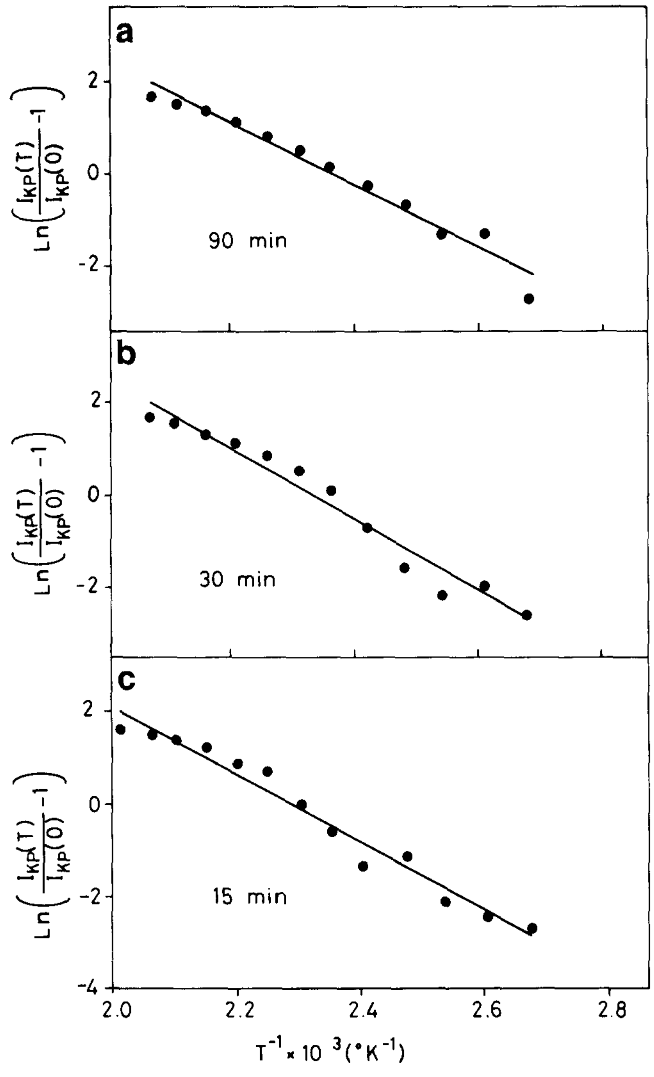

Figure 8 Arrhenius plot of equation (11) for the samples indicated in *Figure 6*. Linear fits are obtained for corrected P intensities above healing temperature (T_H)

time intervals, this relation is written as[23]:

$$\left(\frac{I_{KP}(T)}{I_{KP}(0)}-1\right)=R\exp(-\Delta E_P/2kT) \qquad (11)$$

Here R is the constant related to coefficients in equations (9) and (10). Logarithmic plots of equation (11) for various samples are shown in *Figure 8*. The averaged activation energy of $\Delta E_P = 30\,\mathrm{kcal\,mol^{-1}}$ was obtained from plots where the linear fits were found to be quite satisfactory. Previously, by using the transient fluorescence method a slightly higher activation energy was found (37 kcal mol^{-1}) for PMMA–PIB particles above the glass transition temperature of PMMA[8]. Using the same method the apparent activation energies have been measured as 38, 38.9 and 34 kcal mol^{-1} for the poly(butyl methacrylate) (PBMA) latex particles[12,28,29]. As suggested by Ferry many years ago, these activation energies are characteristic of polymer chain backbone motion[30,31]. Since ΔE_P is the activation energy for the backbone motion and ΔE_P is the healing activation energy of the minor chain (chain segment) for the given temperature range, from the energetic point of view our findings that ΔE_P was three times larger than ΔE_H are quite reasonable.

In conclusion, we have developed here a novel method to measure both healing and diffusion activation energies by using the steady-state fluorescence technique. It is important to note that we measured ΔE_H and ΔE_P without measuring the diffusion coefficients of the diffusing polymer chain; the isothermal experiments needed to determine these coefficients are in progress and will be reported soon.

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