

Photon Transmission Method for Studying Film Formation from Polystyrene Latexes with Different Molecular Weights

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ABSTRACT: A photon-transmission method was used to probe the evolution of transparency during film formation from polystyrene (PS) particles with different molecular weights. The latex films were formed at room temperature from the PS particles having two different average molecular weights and annealed at elevated temperatures in various time intervals above the glass transition (T_g). Onset temperatures (T_H) at given times (τ_H) for the optical clarity of films formed from low (LM) and high molecular (HM) weight PS particles were used to calculate the healing activation energies for the minor chains and found to be 22.0 ± 0.5 and 27.0 ± 0.6 kcal/mol, respectively. The increase in the transmitted photon intensity, I_{tr} , above the T_H was attributed to increase in the number of interfaces that disappeared. The Prager–Tirrell (PT) model was employed to interpret the increase in crossing density at the junction surface. The backbone activation energies (ΔE) were measured and found to be 127.8 ± 2.5 kcal/mol for a diffusing polymer chain across the junction surface for LM and HM latex films. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 866–874, 2000

Key words: polystyrene latex; molecular weight; film formation; photon transmission

INTRODUCTION

Polymer latexes have been utilized in a wide variety of applications in the coating and adhesive technologies, biomedical field, information industry, and microelectronics. In many of these applications, for example, coatings and adhesives, latexes form thin polymer films on a substrate surface. Properties (mechanical, optical, transport, etc.) of the final film should be tailor-made according to the application.

Film formation from latexes is a complicated, multistage phenomenon and depends strongly on the characteristics of colloidal particles. In general, aqueous or nonaqueous dispersions of colloidal particles with the glass transition temperature (T_g) above the drying temperature are called a hard latex dispersion; however, aqueous dispersion of colloidal particles with the T_g below the drying temperature is called a soft latex dispersion. The term “latex film” normally refers to a film formed from soft particles where the forces accompanying the evaporation of water are sufficient to compress and deform the particles into a transparent, void-free film.^{1,2} However, hard latex particles remain essentially discrete and un-

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deformed during the drying process. Film formation from these dispersions can occur in several stages: In both cases, the first stage corresponds to the wet initial state. Evaporation of the solvent leads to a second stage in which the particles from a close-packed array; here, if the particles are soft, they are deformed to polyhedrons. Hard latex, however, stays undeformed at this stage. Annealing of soft particles causes diffusion across particle–particle boundaries, which leads the film to a homogeneous continuous material. In the annealing of the hard latex system, however, deformation of particles first leads to void closure^{3,4} and, then, after the voids disappear, diffusion across particle–particle boundaries begins, that is, the mechanical properties of hard latex films can be developed by annealing, after all solvent has evaporated and all the voids have disappeared.

After the void-closure process is completed, the mechanism of film formation, by annealing of hard latex films, is known as interdiffusion of polymer chains followed by healing at the polymer–polymer interface. In general, when two identical polymeric materials 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, we may say that the junction has “healed.” Many years ago, Voyutskii⁵ 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 essentially 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 wormlike motion described by the reptation model, proposed by de Gennes.⁶ 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 Tirrell⁷

derived a relation for the crossing density of the chains by using the reptation model during the healing process. Wool and O'Connor⁸ 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.

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 particle boundaries disappeared over time, but in other cases, the boundaries persisted for months. It was suggested that, in the former case, particle boundaries were 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 annealed¹¹ 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^{12,13} in conjunction with latex particles labeled with donor and acceptor chromophores. The steady-state fluorescence (SSF) method combined with DET was also used for studying film formation from hard latex particles.^{14–17} Extensive review of the subject is given in ref. 18. Recently, various experiments with the photon transmission method using a UV-visible (UVV) spectrophotometer were performed to study latex film formation from PMMA and PS latexes where void closure and interdiffusion processes at the junction surfaces were studied.^{19–22} These studies all indicate that annealing leads to polymer diffusion and mixing as the particle junction heals during latex film formation.

In this study, monodisperse polystyrene (PS) latexes having an average diameter of 2 μm were produced by a dispersion polymerization technique using an ethanol/water mixture as a dispersion medium. Poly(vinyl pyrrolidone) (PVP) and 2,2-azobisisobutyronitrile (AIBN) were employed as a steric stabilizer and a disperse-phase soluble initiator, respectively. Two different initiator concentrations were used in the polymerization recipe in order to achieve PS latexes having two

different molecular weights without causing any change in the final particle diameter. Transparencies of the films formed from these PS latexes with high (HM) and low (LM) molecular weights were studied by measuring the transmitted photon intensities (I_{tr}) using an UV-visible spectrophotometer. Various stages of film formation were generated by annealing the dried latex powders at equal time intervals above the glass transition temperature, T_g , of PS. Variations in I_{tr} with respect to annealing temperature were used to study the healing and interdiffusion processes at the particle–particle junction. Onset temperatures at given times for the increase in I_{tr} were attributed to the healing temperature (T_H) and healing time (τ_H) and were used to measure the activation energies (ΔE_H) for the randomized polymer chain segments (minor chains) across the junction surface. Above the T_H , the increase in I_{tr} at elevated temperature was explained by the interdiffusion of polymer chains. The method developed by Prager and Tirrell (PT)⁷ was employed to investigate the interdiffusion processes at the junction surfaces. Activation energies (ΔE) for diffusing polymer chains were measured and found to be five times larger than the healing activation energies for the corresponding LM and HM films. ΔE was attributed to the backbone motion of the PS chain.

EXPERIMENTAL

The monomer, styrene (S) (Yarpet A.S., Ýzmit, Turkey), was treated with aqueous NaOH to remove the inhibitor and stored in a refrigerator until use. The initiator was AIBN (BDH Chemicals Ltd., Poole, UK). An ethyl alcohol (Merck, Darmstad, Germany)/water mixture was used as the dispersion medium. PVP; 30 K, Fluka, Switzerland) was used as a steric stabilizer.

Polymerizations were carried out in a magnetic-driven, sealed, cylindrical reactor equipped with a temperature-control system.^{23,24} One gram of the steric stabilizer was dissolved in the dispersion medium containing 90 mL of ethyl alcohol and 10 mL of water. The monomer phase was prepared by dissolving various amounts of AIBN (70 and 140 mg for HM and LM PS latexes, respectively) in 10 mL of styrene. These two phases were mixed and charged to the reactor agitated with an anchor-type agitator at a speed of 150 rpm, and the polymerization was conducted at 80°C for 24 h.

The PS latex was first cleaned using a serum-replacement technique as also given in previous publications.^{23,24} The latex from the reactor was centrifuged and the supernatant was removed. The particles were washed with fresh dispersion medium a few times, then distilled water was added and a new dispersion was stirred for 24 h at room temperature to remove any stabilizer remaining on the surface of the polymeric particles. The PS latex was treated with a mixed bed of anion- and cation-exchange resins (H^+ and OH^- type, Amberlite, BDH) at the last step.

The average particle size of each type of PS particles was evaluated using scanning electron micrographs. The latex solution was spread onto a metal disk and the solvent (i.e., water and alcohol) was evaporated. The dried beads were coated with a thin layer of gold (about 100 Å) in a vacuum. Three separate photographs (each containing 100–300 beads) were taken for each latex sample with 2000–2600 magnification using a scanning electron microscope (SEM, JEOL, JEM1200EX, Japan). The size of the beads was measured on photographs and checked using calibration samples.

The average molecular weights of the PSs were determined by a GPC system (Waters, USA). The GPC unit, consisting of Waters Model 510 HPLC pump and a Waters U6K injector, was equipped with two Ultrastyrigel columns (Waters, 10 and 500 Å) in series and a Waters 486 tunable absorbance detector. Chloroform was used both as the solvent and the eluent. Elution was performed at a temperature of 30°C and at a flow rate of 1 mL/min using a Waters 510 HPLC pump. The columns were calibrated with PS standards (Shodex standards, SL-105, Showa Denko, Japan). Molecular weights of PS for LM and HM particles were found to be 3.6×10^4 and 9.1×10^4 g/mol, respectively.

Latex film preparation was carried out by dispersing PS particles in water in a test tube with the solid content taken as 1%. Films were prepared from the dispersion of particles by placing a different number of drops on glass plates of size 0.9×3.2 cm² and allowing the water to evaporate. Here, attention was paid to that the water dispersion from the droplets has to cover the whole surface area of the plate and remain there until the water has evaporated. Samples were weighed before and after the film casting to determine the film thicknesses. Average size for the particles was taken to be 2 μm to calculate the number of layers in the films. Glass plates before

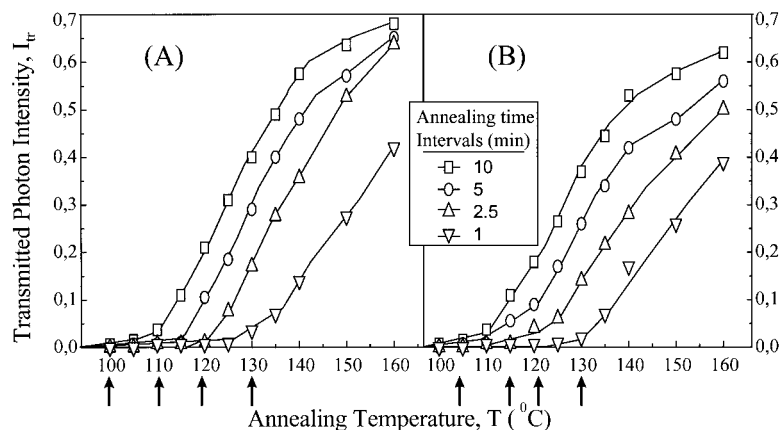


Figure 1 Plot of transmitted photon intensity I_{tr} versus annealing temperature for the latex films: (A) LM; (B) HM. Onset temperatures are shown by arrows.

and after film casting were cleaned with acetone and dried completely before using.

In this work, UVV experiments were carried out with the annealed LM and HM latex film samples. The annealing process of the latex films was performed in an oven in air above the T_g of PS after the evaporation of water, in 1-, 2.5-, 5-, and 10-min time intervals at elevated temperatures between 100 and 160°C. The temperature was maintained within $\pm 1^\circ\text{C}$ during annealing. After annealing, each sample was placed in a UVV spectrophotometer (Lambda 2S of Perkin-Elmer, USA) and transmission was detected between 300 and 400 nm. Another glass plate was used as a standard for all the UVV experiments. All measurements were carried out at room temperature after the annealing process was completed.

RESULTS AND DISCUSSION

Healing at Particle-Particle Junction

Transmitted photon intensities from the LM and HM films are plotted versus annealing temperature for various time intervals in Figure 1(A,B), respectively. It is seen that all the I_{tr} intensity curves start to increase around 100°C, which is around the T_g (105°C) of PS with increasing annealing temperature. Relatively small I_{tr} intensities are observed for latex films annealed at short time intervals, indicating that some photons dissipate, that is, cannot reach the photodiode after they pass through these films. It was observed that in increasing the annealing time from 1 and

2.5 min to 5 and 10 min for increasing the annealing temperature that I_{tr} becomes larger. These changes in I_{tr} may be interpreted as that annealing the films for longer times results in the formation of more transparent films.

It is seen in Figure 1(A,B) that onset temperatures, T_H , for the increase in I_{tr} values shifted to higher temperatures for smaller annealing time intervals for both the LM and HM samples. In Figure 2(A,B), T_H values are plotted versus corresponding annealing time intervals, τ_H , for LM and HM films, respectively, and it is observed that as τ_H decreases, T_H values increase. These behaviors for each experimental set (LM and HM) 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 onset temperature might correspond to the “healing temperature (T_H)” for a given “healing time (τ_H)” at which the polymer chain presumably moves halfway across the junction surface.⁷ For instance, at 100, 110, 120, and 130°C, τ_H values were found to be 10, 5, 2.5, and 1 min, respectively, for the LM samples. For a given τ_H and T_H , particle boundaries start to disappear during coalescence and, consequently, the latex film starts to become transparent to the light; as a result, the transmitted intensity starts to increase. Initially, below T_H , due to the sharp particle boundaries or voids between particles, light scatters from the film surface. Increasing of temperature causes wetting and initiates segmental motion, and as a result, polymer chain segments move across the interface. Subsequently, more light can enter the latex

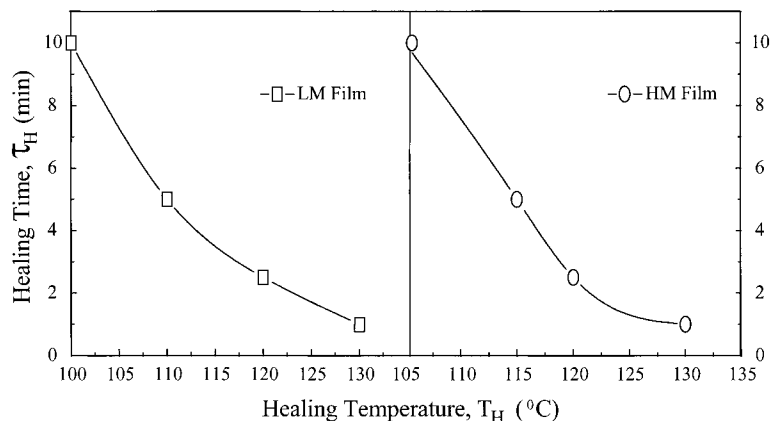


Figure 2 Plot of healing temperature T_H versus healing time τ_H for LM and HM film samples.

film and the transmission intensity starts to increase.

To quantify the above results, the minor chain model developed by Wool et al.^{25,26} was employed. They used the reptation model of chain dynamics⁶ where, by a wriggling motion, a chain, on average, moves coherently back and forth along the center 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 $l(t)$ (see Fig. 3). The conformations of the minor chains are always Gaussian. Kim and Wool²⁵ de-

rived the average of the $l(t)$ values for times shorter than the tube renewal time (T_r) and found that

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

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

$$D = D_0 \exp(-\Delta E_H/kT_H) \quad (2)$$

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 the $\langle l^2 \rangle$ values are identical at the healing temperatures of each separate set of experiments, then a very useful relation can be obtained from eqs. (1) and (2):

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

where $B = \langle l^2 \rangle / 2D_0$ is a constant for all sets of experiments in Figure 2. The logarithmic form of eq. (3) is plotted in Figure 4(A,B) and $\Delta E_H = 22.0 \pm 0.5$ and 27.0 ± 0.6 kcal/mol were found for the LM and HM films, respectively. These activation energies are much smaller than were the activation energies found for the backbone motion for the PS particles stabilized with PVP and PAA²¹ (150 and 200 kcal/mol, respectively) during film formation.²¹ After complete wetting, it is not unreasonable to accept that the energy requirement for a minor chain to cross the junction surface is

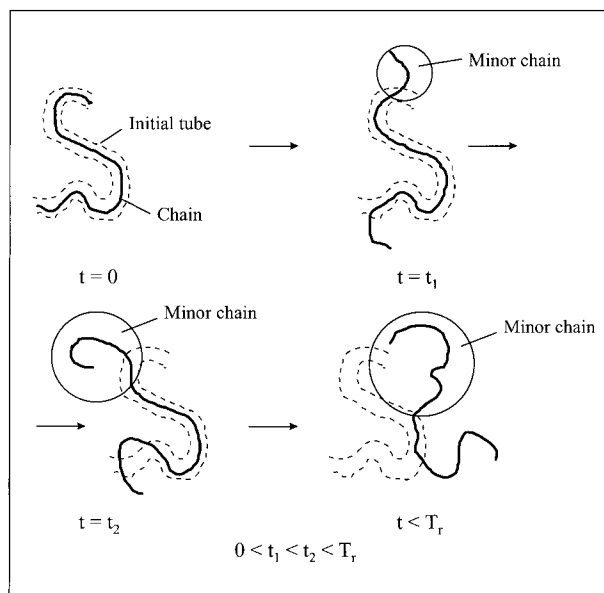


Figure 3 Disengagement of a Gaussian chain from its initial tube in the reptation model, that is, the growth of a minor chain.

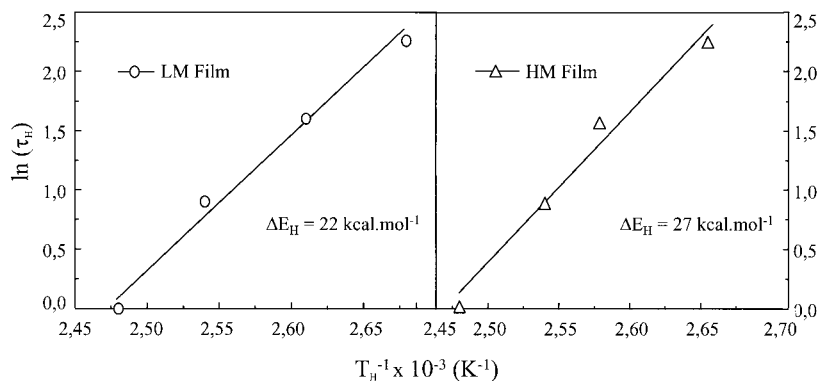


Figure 4 Arrhenius plot of eq. (3). ΔE_H is the healing activation energy in kcal mol⁻¹ for LM and HM film samples.

much less than is the diffusion energy of a backbone in a bulk polymer.

Interdiffusion of Polymer Chains

Figure 5(A,B) compares the transparencies of LM and HM films for 10 and 2.5 min of annealing as a function of annealing temperature where the I_{tr} of the HM films present at least 40% smaller values than those of the LM films in both cases. Here, delay in film formation is observed for the high molecular weight PS particles, which is expected due to slower diffusion of large polymer chains. The bad quality of films for the HM samples is related to the delay in film formation at this temperature region. The transparency of the films can be explained by knowing that homogeneous media do not scatter light. In other words, lattice heterogeneities cause the scattering of light, as a result, transmitted photon intensity

decreases in heterogeneous film compared to homogeneous ones. To interpret the temperature behavior of I_{tr} intensities, a simple rectangular lattice model can be used to simulate the latex film formation process.²¹ A rectangular lattice is divided into squares with side length, and the centers of the squares are taken as refraction centers for photons traveling in the lattice. The distance of a photon between each consecutive collision is defined as the mean free path, $\langle r \rangle$, of a photon during its journey in the lattice. Boundaries between squares are randomly removed to simulate the disappearance of particle–particle interfaces during the annealing process of the film. In this picture, the early stage of annealing can be simulated by a rectangular lattice where a photon has short $\langle r \rangle$. As more boundaries are removed between the square compartments in the lattice, $\langle r \rangle$ values increase, which simulates the

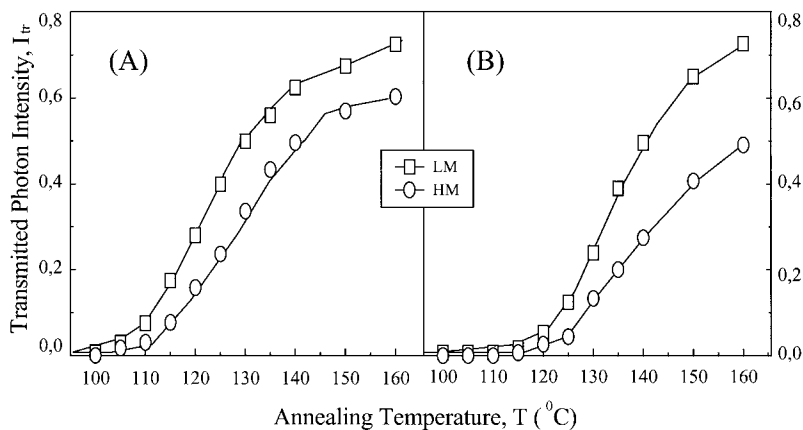


Figure 5 Comparison of the I_{tr} values of LM and HM samples annealed for (A) 10 and (B) 2.5-min time intervals.

latter stage of annealing. As boundaries are continuously removed, $\langle r \rangle$ values increase and more photons can be transmitted from the lattice, which indicates that annealing causes high transparency.²¹ When the number of photons transmitted from the back surface is named N_{tr} , it can be seen that as the boundaries between the squares are removed, N_{tr} increases, which corresponds to an increase in transparency of the latex film as it is annealed.

When film samples were annealed at elevated temperatures for various time intervals, a continuous increase in I_{tr} intensities was observed until they become saturated. The increase in I_{tr} was already explained in the previous paragraph, by the increase in the transparency of latex film due to the disappearance of particle-particle interfaces. As the annealing temperature is increased, some part of the polymer chains may cross the junction surface and particle boundaries start to disappear, and as a result, the transmitted photon intensity I_{tr} increases, presenting a similarity to N_{tr} .²¹ Here, a shorter annealing time and larger molecular weight results in bad-quality films during the film formation process due to slower diffusion of long polymer chains.

To quantify these results, the PT model⁷ for the chain-crossing density was employed. These authors used de Gennes' "reptation" model⁶ to explain configurational relaxation at the polymer-polymer junction where each polymer chain is considered to be confined to a tube in which it executes a random back-and-forth motion. A homopolymer chain with N freely jointed segments of length L was considered by PT, which moves

back and forth by one segment with a frequency ν . In time, the chain is displaced down the tube by a number of segments, m . Here, $\nu/2$ is called the "diffusion coefficient" of m in one-dimensional motion. PT calculated the probability of the net displacement with m during time t in the range of $n - \Delta$ to $n - (\Delta + d\Delta)$ segments. A Gaussian probability density was obtained for small times and large N . The total "crossing density" $\sigma(t)$ (chains per unit area) at the junction surface then was calculated from the contributions due to chains still retaining some portion of their initial tubes, plus a remainder, $\sigma_1(t)$. Here, the $\sigma_2(t)$ contribution comes from chains which have relaxed at least once. In terms of reduced time $\tau = 2\nu t/N^2$, the total crossing density can be written as

$$\sigma(\tau)/\sigma(\infty) = 2\pi^{-1/2} \left[\tau^{1/2} + 2 \sum_{k=0}^{\infty} (-1)^k \times [\tau^{1/2} \exp(-k^2/\tau) - \pi^{-1/2} \operatorname{erfc}(k/\tau^{1/2})] \right] \quad (4)$$

For small τ values, the summation term in the above equation is very small and can be neglected, which then results in

$$\sigma(\tau)/\sigma(\infty) = 2\pi^{-1/2} \tau^{1/2} \quad (5)$$

This was predicted by de Gennes on the basis of scaling arguments. To compare our results with the crossing density of the PT model, the temper-

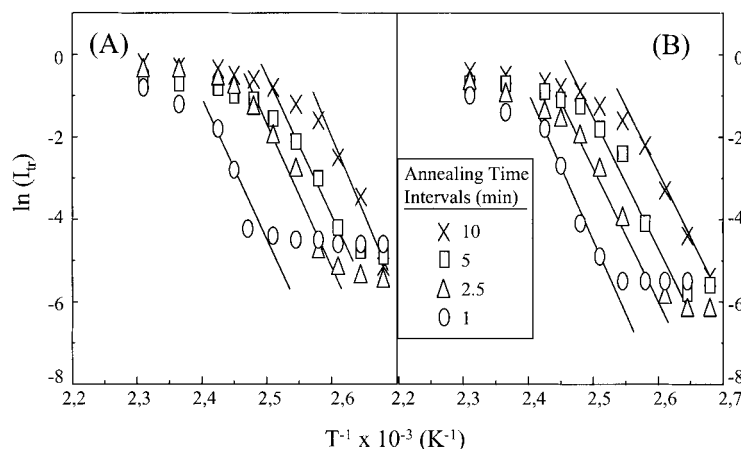


Figure 6 Logarithmic plots of I_{tr} data from Figure 1 versus inverse annealing temperature (T^{-1}) for (A) LM and (B) HM. Data are fitted to eq. (8) to produce ΔE values.

Table I Experimentally Observed ΔE Values in Various Time Intervals of Annealing

Film	Time (min)				
	1	2.5	5	10	Averaged
LM (3.6×10^4)	121.2 ± 2.5	132.5 ± 2.5	132.0 ± 2.5	134.2 ± 2.5	130.0 ± 2.5
HM (9.1×10^4)	125.7 ± 2.5	125.2 ± 2.5	125.0 ± 2.5	126.7 ± 2.5	125.6 ± 2.5

ΔE values were found by fitting the I_{tr} data to eq. (8). Energy units are in kcal/mol. The last column gives the average ΔE values. The molecular weight of PS particles are given in the parentheses.

ature dependence of $\sigma(\tau)/\sigma(\infty)$ can be modeled by taking into account the following Arrhenius relation for the linear diffusion coefficient:

$$\nu = \nu_0 \exp(-\Delta E/kT) \quad (6)$$

Here, ΔE is defined as the activation energy for the back-and-forth motion. By combining eqs. (5) and (6), a useful relation is obtained as

$$\sigma(T)/\sigma(\infty) = A \exp(-\Delta E/2kT) \quad (7)$$

where $A = (8\nu_0 t / \pi N^2)^{1/2}$ is a temperature-independent coefficient.

The increase in I_{tr} is already related to the disappearance of particle–particle interfaces, that is, as annealing temperature is increased, more chains relaxed across the junction surface, and as a result, the crossing density increases. Now, if it can be assumed that I_{tr} is proportional to the crossing density $\sigma(T)$, then the phenomenological equation can be written as

$$I_{tr}(T)/I_{tr}(\infty) = A \exp(-\Delta E/2kT) \quad (8)$$

Logarithmic plots of I_{tr} versus T^{-1} are presented in Figure 6(A,B) for the LM and HM films, respectively. The activation energies, ΔE , are produced by fitting the data to logarithmic form of eq. (8) and are listed in Table I. It has to be noted that the observed ΔE values are independent of the molecular weight and time interval in which latex film is annealed.

In conclusion, back-and-forth activation energies (ΔE) for LM and HM films were found to be six times larger than the healing activation energies (ΔE_H) for the minor chains for the corresponding samples; it is quite reasonable to accept that a small-chain segment (minor chain) needs much less energy to execute its motion than a chain segment needs to execute its back-and-forth motion in the middle of the long chain. Here, one has to notice that healing and interdiffusion processes, in fact, correspond to two different diffusion regimes. In other words, during healing,²⁵

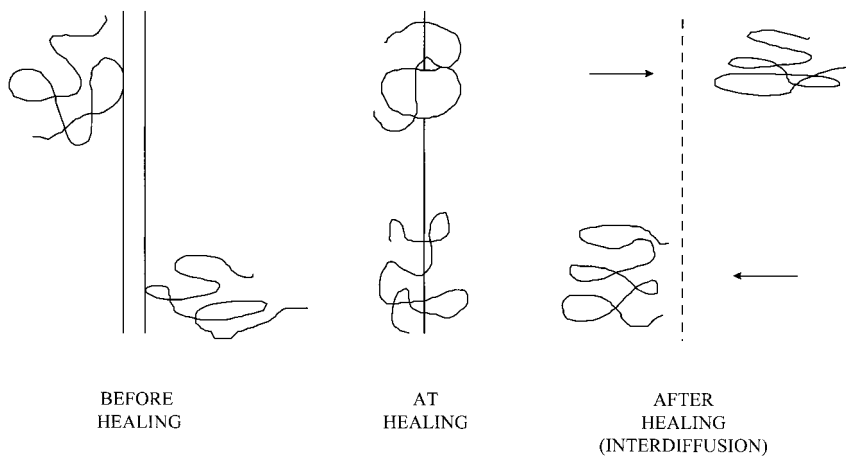


Figure 7 Schematic representation of the healing and interdiffusion phenomenon at the particle–particle junction before and after healing.

the number of random-coil chains intersecting the unit area of the interface behaves with time as $t^{1/4}$; however, during interdiffusion,⁷ the number of chains crossing the unit area of the interface behaves with time as $t^{1/2}$. Figure 7 summarizes the whole picture for the healing and interdiffusion processes at the particle–particle junction, where healing occurs around the onset temperature (T_H) at which minor chains cross the junction surface. Above T_H , interdiffusion starts and increases as the annealing temperature is increased.

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