

# Effects of Aging on Latex Film Formation from Polystyrene Particles: A Photon Transmission Study

ÖNDER PEKCAN,<sup>1</sup> ERTAN ARDA,<sup>2,3</sup> KEMAL KESENCİ,<sup>4</sup> ERHAN PIŞKİN<sup>4</sup>

<sup>1</sup> İstanbul Technical University, Department of Physics, Maslak, 80626 İstanbul, Turkey

<sup>2</sup> Trakya University, Department of Physics, 22030 Edirne, Turkey

<sup>3</sup> International Center for Physics and Mathematics, P. K. 126, 22030 Edirne, Turkey

<sup>4</sup> Hacettepe University, Chemical Engineering Department and Bioengineering Division, Beytepe, 06532 Ankara, Turkey

Received 21 January 2000; accepted 8 June 2000

**ABSTRACT:** Aging due to the storage time on latex film formation was studied using the photon transmission method. The UV visible technique was used to monitor the evolution of transparency during film formation from two different polystyrene (PS) particles produced by using two different steric stabilizers, i.e., polyvinyl alcohol and polyvinyl pyrrolidone. The latex films were prepared from PS particles at room temperature before and after aging and annealed at elevated temperatures in various time intervals above glass transition ( $T_g$ ). The increase in the transmitted photon intensity  $I_{tr}$  was attributed to the increase in the number of disappeared particle–particle interfaces. Relative decrease in transparency and delay in film formation were observed in the aged latex films compared to the nonaged ones. The Prager–Tirrell model was employed to interpret the increase in crossing density at the junction surface. The back and forth activation energies ( $\Delta E$ ) were measured and found to be dependent on aging for a diffusing polymer chain across the junction surface. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 79: 2014–2021, 2001

**Key words:** polystyrene latexes; stabilizer type; aging; film formation; photon transmission

## INTRODUCTION

Chemical and physical aging are important processes for the film formation from latex particles that determine the properties of a coating including its durability. Physical aging occurs in all polymeric materials stored at a temperature below their glass transition temperature ( $T_g$ ), which is a reversible process by heating the material at a temperature above  $T_g$ . Physical aging can be

achieved by cooling the polymer from a temperature above  $T_g$  to one below it, which brings a polymer to a nonequilibrium state since the values of volume, enthalpy, and entropy are higher than in equilibrium state.<sup>1</sup> In fact, physical aging is a process of many terms related to volume, enthalpy, and structural relaxations. On the other hand, chemical aging includes irreversible composition changes induced in a polymeric material by temperature, moisture, and photooxidation.

In the past few years, water-based polymer latexes have gained more attention in the coating and adhesives industries over conventional sol-

---

Correspondence to: E. Pişkin.

*Journal of Applied Polymer Science*, Vol. 79, 2014–2021 (2001)  
© 2001 John Wiley & Sons, Inc.

vent-based systems, mainly due to restrictions imposed by environmental requirements. The mechanical properties of latex films are dependent on the molecular weight and its distribution,<sup>2,3</sup> and are sensitive to stabilizers<sup>4</sup> and surfactants.<sup>5</sup> In addition, the quality of these films, for a given molecular weight, depends on the annealing time and annealing temperature.<sup>6–9</sup>

Several stages during film formation have been observed experimentally and a phenomenological description of the process can be divided into the three following steps<sup>10</sup>: (1) Water evaporation and colloid concentration—as water evaporates, a uniform shrinkage of the interparticle distance occurs and the voids are gradually filled by particle sliding, until a dense packing of spheres is obtained. (2) Particle deformation and evaporation of the bounded water—this stage, also called coalescence, results in a honey can like structure of deformed particles. (3) Interdiffusion of macromolecules—in this stage the mechanical strength increased and the water permeability of the film decreases. Under certain conditions the polymer chains can diffuse through the particle boundaries and an homogeneous, continuous film is formed.

The research on diffusion across polymer–polymer interfaces started with the pioneering work of Voyutskii.<sup>11</sup> In general, when two identical polymeric materials are brought into intimate contact and heated at a temperature above the glass transition, the polymer chains become mobile, and interdiffusion of polymer chains across the interface can occur. After this process the junction surface become indistinguishable in all respects from any other surface that might be located in the polymeric material. This process is called “healing of the junction” at which the joint achieves the same cohesive strength as the bulk polymeric material. The word “interdiffusion” in polymer science is used for the process of mixing, intermingling, and homogenization at the molecular level, which implies diffusion among polymer chains. In the bulk state, polymer chains have a Gaussian distribution of segments. Chains confined to the half space adjacent to the junction have distorted conformations.<sup>12–14</sup> Diffusion across the junction leads to configurational relaxation and recovery of Gaussian chain behavior. Polymers much larger than a certain length are often pictured as confined to a tube, and diffusion occurs by a reptile-like motion. In this model, each polymer chain is confined to a tube along the length of which it executes a random back and forth mo-

tion. This reptile-like motion will cause the chain to slip out of a section of tube at one end or the other. The reptation time ( $T_R$ ) describes the time necessary for a polymer to diffuse a sufficient distance for all memory of the initial tube to be lost. This is the time it takes for initial configuration to be forgotten and the first relaxation to be completed.

Small-angle neutron scattering (SANS) has been used to study latex film formation at the molecular level. Extensive studies using SANS have been performed by Sperling and co-workers on compression-molded polystyrene film.<sup>15</sup> Direct-nonradiative energy transfer (DET) method has been employed to investigate the film formation process from dye-labeled polymeric particles.<sup>16–18</sup> The steady state fluorescence technique combined with DET has been used to examine healing and interdiffusion processes in the dye-labeled polymethylmethacrylate (PMMA) latex systems.<sup>19,20</sup> Recently photon transmission method has been performed to study latex film formation from PMMA and polystyrene (PS) particles, using the UV-visible (UVV) technique as a function temperature and time.<sup>21–23</sup>

In this study, PS latexes were produced by dispersion polymerization of the monomer (styrene) in an ethanol/water mixture. Polyvinyl alcohol (PVA) or polyvinyl pyrrolidone (PVP) were used as steric stabilizers with a disperse phase soluble initiator (i.e., 2,2-azobisisobutyronitrile). This work aims to study the effect of storage time on latex film formation from PS latexes. Transparencies of the films formed from these PS latexes were monitored by measuring the transmitted photon intensities ( $I_{tr}$ ) by using a UVV spectrophotometer. With increasing aging (storage time) delay in film formation and a relative decrease in the transparency were observed. The method developed by Prager and Tirrell (PT)<sup>13</sup> was employed to investigate the healing processes at the junction surfaces of the these films.

## MATERIALS AND METHODS

### Preparation of PS Latexes

The monomer, styrene (S) (Yarpet A.S., Turkey), was treated with aqueous NaOH to remove the inhibitor and stored in a refrigerator until use. The initiator was 2,2-azobisisobutyronitrile (AIBN) (BDH Chemicals Ltd., UK). Ethyl alcohol (Merck, Germany)/water mixture were used as

the dispersion medium. PVA (MW: 50,000, Aldrich, USA) and PVP (MW: 60,000, Fluka, Switzerland) were used as steric stabilizers.

Polymerization were carried out in a magnetic-driven, sealed, cylindrical reactor equipped with a temperature-control system.<sup>24,25</sup> Two grams of the steric stabilizer was dissolved in the dispersion medium containing 180 mL of ethyl alcohol and 20 mL of water. The monomer phase was prepared by dissolving 0.28 g AIBN in 20 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 cleaned first using a serum replacement as also given in our previous publications.<sup>24,25</sup> The latex from the reactor was centrifuged and the supernatant was removed. The particles were washed with fresh dispersion medium 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<sup>+</sup> and OH<sup>-</sup> type, Amberlite, BDH) at the last step.

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 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 beads was measured on photographs and checked using calibration samples.

The average molecular weights of polystyrenes produced with different stabilizers were determined by a gas permeation chromatography (GPC) system (Waters, USA). The GPC unit, consisting of Waters Model 510 high performance liquid chromatography pump and Waters U6K injector, was equipped with two Ultrastryagel columns (Waters, 10 and 500 Å) in series and Water 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 polystyrene standards (Shodex Standards, SL-105, Showa Denko, Japan). Molecular weights, measured before and after aging for 10 months, are

**Table I** Number Average Molecular Weights of Polystyrene Produced with Two Different Stabilizers Before and After Aging for 10 Months

Stabilizer Type	MW <sub>n</sub> (Before Aging)	MW <sub>n</sub> (After Aging)
PVA	$1.5 \times 10^4$	$2.2 \times 10^4$
PVP	$1.8 \times 10^4$	$2.9 \times 10^4$

given in Table I, where it is seen that MW are increased due to aging.

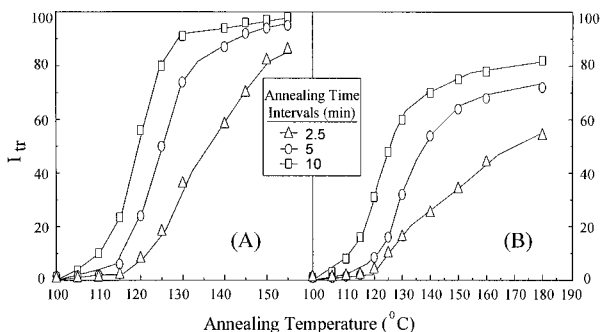
### Film Preparation and UVV Measurements

Films were prepared before and after aging for 10 months the polystyrene latexes prepared with two different stabilizers, i.e., PVA and PVP, by placing different numbers of drops of latex on glass plates (with the size of  $0.9 \times 3.2 \text{ cm}^2$ ) and allowing the water to evaporate at room temperature. Here we were careful to ensure that the liquid dispersion from droplets covers the whole surface area of the plates and remains there until the water has evaporated.

In this work UVV experiments were carried out with annealed latex samples. Annealing process of the latex films was performed above the  $T_g$  of PS after evaporation of water, in 2.5, 5, 10, 15, and 25 min time intervals at elevated temperatures between 100 and 155°C before aging and between 100 and 180°C after aging. The temperature was maintained within  $\pm 1^\circ\text{C}$  during annealing. After annealing, transmissions of the films were detected with an UVV spectrophotometer (Lambda 2S of Perkin Elmer, USA) at a wavelength between 300 and 400 nm at room temperature. A glass plate was used as a standard for all UVV experiments.

## RESULTS AND DISCUSSION

In this work PS latexes were produced by dispersion polymerization of styrene in a medium composed of an ethanol/water mixture by using steric stabilizers. PVA or PVP was used as a steric stabilizer with a disperse phase soluble initiator (i.e., AIBN). With the recipe used, monosize PS particles with an average diameters around of  $2.0 \mu\text{m}$  were obtained.



**Figure 1** Plot of transmitted photon intensity  $I_{tr}$  versus annealing temperature at various time intervals for the PVP latex films: (A) before and (B) after aging of 10 months. Numbers on each curve indicate annealing times.

The number average molecular weights ( $MW_n$ ) of polystyrenes produced with two different stabilizers (i.e., PVA and PVP), which were determined by using the GPC data, before and after aging are given in Table I. As seen here, the average molecular weights of the polystyrenes were in the same order but changed with the stabilizer type and increased aging for 10 months.

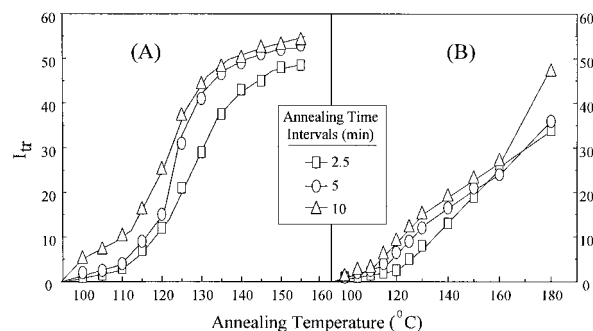
In this study, the type of stabilizer and aging were selected as the critical parameters of focus. It is known that the stabilizer plays an important role in the dispersion polymerization process.<sup>24–27</sup> The stabilizer determines both the particle stability during the particle formation step and the viscosity of the continuous medium. A graft copolymer (i.e., polymeric stabilizer-g-polystyrene) can be formed *in situ* during the particle formation stage when a precursor polymer (i.e., PVP or PVA) that contains proper active sites for chain transfer of the oligomeric radicals is used as a stabilizer. The formation of graft copolymer during the dispersion polymerization is a complex process. The structure and concentration of the precursor polymer control the rate of formation, concentration, and the properties of the graft copolymer. The formed graft copolymer and the precursor polymer are both absorbed competitively onto the surface of the resultant polymer particles. Note that the adsorption of the stabilizer molecules on the particle surface is described as the physical adsorption, which is rather weak and reversible, which means that it can be removed from the surface by a careful cleaning procedure. However, the adsorption of graft copolymer (which carries the stabilizer molecules) are termed “anchorage adsorption” (in-

cluding chemical bound and strongly entrapped graft copolymer molecules on the surface), which means these molecules cannot easily be removed from the particle surfaces.

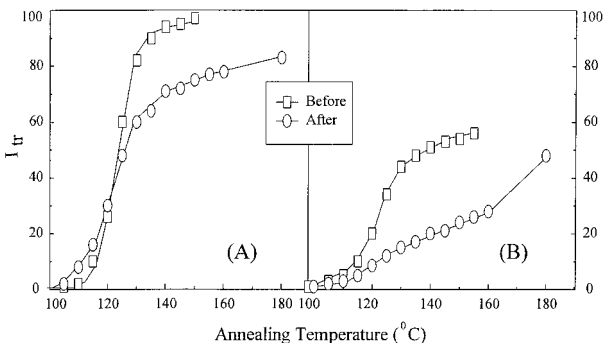
From the above discussion one can easily draw the conclusion that the surface chemistry of the PS latex particles would be different when one uses different stabilizer molecules in the dispersion polymerization. This also means that the film formation of the latexes carrying different stabilizer molecules (most probably chemically attached) on their surfaces would be different, which was the main question to be addressed in this study. Another parameter that effects the film formation process is the storage time, which is probably caused by chemical aging of the latex material. The results related to film formation from nonaged and aged latexes are discussed in the following sections. Note that, for convenience, the films formed from the PS latexes prepared with different stabilizers are called by the stabilizer name, i.e., “the PVA or PVP films,” in the rest of this article.

### Aging and Transparency of Latex Film

Transmitted photon intensities  $I_{tr}$  from the PVP and PVA films made before and after aging are plotted versus annealing temperature for various time intervals in Figure 1(A,B) and Figure 2(A,B) respectively. It can be seen that all  $I_{tr}$  intensity curves start to increase around 110°C, which is above  $T_g$  (105°C) of PS with increasing annealing temperature. Relatively small  $I_{tr}$  intensities are observed in latex films annealed at short time intervals (2.5 and 5 min), indicating that photons



**Figure 2** Plot of transmitted photon intensity  $I_{tr}$  versus annealing temperature at various time intervals for the PVA latex films: (A) before and (B) after aging of 10 months. Numbers on each curve indicate annealing times.



**Figure 3** Comparison of  $I_{tr}$  data of A-PVP and B-PVA for 10 min. Annealing before and after aging of 10 months.

cannot reach the photodiode after they pass through these films. It was observed that  $I_{tr}$  becomes larger by an increase in the annealing time interval. These changes in  $I_{tr}$  may be interpreted that annealing the films for larger times result in the formation of more transparent films.

It can be seen from Figure 1(A) that PVP films prepared from nonaged particles can form 95% transparent films when they are annealed around 150°C for 5 and 10 min. However, Figure 2(A) shows that the nonaged PVA films can form only 55% transparent films when they are annealed around the same temperature for 5 and 10 min. Figure 1(B) and 2(B) present the  $I_{tr}$  data from the PVP and PVA films prepared from the aged particles for 10 months, where it is seen that the PVP film needs higher temperature to reach a plateau compared to nonaged films. On the other hand, PVA films prepared from aged particles unable to reach a plateau even they are annealed at 180°C. Figure 3(A and B) compare the  $I_{tr}$  data of PVP and PVA for the aged and nonaged samples for 10 min annealing time interval.

The transparency of the films can be explained by knowing that homogeneous media do not scatter light. In other words, lattice heterogeneities cause scattering of light; as a result, transmitted photon intensity decreases in heterogeneous latexes compared to the homogeneous ones. The average diameters of all PS latexes were very close to each other and were around 2  $\mu\text{m}$ . Therefore the difference in the extent of homogeneity of the PVP and PVA films mentioned above cannot result from the size differences of latex particles. Table I shows that the average molecular weights of the PS produced with different stabilizers are different (but not very significantly). If we consider only the molecular weights, we expect a

higher transparency from the latex prepared with PVA, which has a lower molecular weight. Here we assume that short polymer chains move easier than longer chains, which leads faster coalescence of the particles, and therefore better transparency. However, this is not the case here. The average chain length of PVP (which forms a more homogeneous film) is larger than the chain lengths of the other one (which forms more heterogeneous films). Therefore, the variation in homogeneities of the latex films cannot be due to the differences in the average molecular weights of PS. On the other hand, an increase in the molecular weight of PS due to aging creates more heterogeneous films than nonaged films. After aging, delays in the film formation are also observed, especially for PVA particles.

We can also consider the effects of  $T_g$  values of the stabilizer molecules located at the surface of the particles. The  $T_g$  values of PVP and PVA are 327 and 358 K, respectively.<sup>28</sup> The PS particles prepared with PVP (which have a lower  $T_g$  than PVA) may lead to easier coalescence of the particles, and resulting films with higher transparencies, as we obtained, both in the aged and nonaged samples.

One further explanation may be the compatibility of these polymeric stabilizers with the forming polystyrene chains during the dispersion polymerization. The solubility parameters obtained by different methods for PS, PVA, and PVP are 8.5–9.1, 12.6, and 10.1–11.8 (cal/cm<sup>3</sup>)<sup>1/2</sup>, respectively.<sup>28</sup> As seen here, the solubility parameter of PVP is closer to that of PS than of PVA—in other terms, PVP is more compatible with PS than PVA. Higher compatibility may result in particle surfaces where more polystyrene molecules may be located on the surface (in parallel, more stabilizer molecules penetrate from the surface to the bulk). Because of this, the particles prepared with PVP form films with higher transparencies than those prepared with PVA.

We may conclude the above discussions by saying that the polymeric particles with smaller average molecular weights, prepared with more compatible stabilizers with lower  $T_g$  values, form films with high transparencies for the nonaged and aged latex particles.

The temperature behavior of  $I_{tr}$  intensities was explained by a simple rectangular lattice model that is used to simulate the latex film formation process.<sup>4</sup> A rectangular lattice is divided into squares with side length, and the center of the squares are taken as refraction centers for pho-

tons 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 a  $\langle r \rangle$ . As more boundaries are removed between the square compartments in the lattice,  $\langle r \rangle$  values increase, which simulates the 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.<sup>4</sup>

Here, even though all the interfaces between particles are removed, the PVA film exhibit lower transparencies than the PVP film; i.e., the PVA films cannot attain complete homogeneity due to incompatibilities between PS and PVA stabilizers, both for the nonaged and aged samples. Most probably phase separation occurs between these polymeric materials, and domain sizes of these two phases are on the order of the wavelength of light and scatter light tremendously giving opacity to these latex films. On the other hand, high compatibility between PS and PVP produces nice homogeneous latex films after all the particle–particle interfaces have disappeared, especially for the nonaged films.

### Interdiffusion and Activation Energies Before and After Aging

When film samples prepared from the aged and nonaged PS particles were annealed at elevated temperatures for various time intervals, a continuous increasing  $I_{tr}$  intensities was detected. The increase in  $I_{tr}$  was already explained in the previous section by the increase 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 in both the aged and nonaged samples.

In order to interpret these results, the PT-model<sup>13</sup> for the chain interdiffusion was employed,<sup>4</sup> where the total crossing density can be written for small reduced times  $\tau = 2 \nu t/N^2$  as

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

Here  $N$  is the number of freely jointed segment in and  $\nu$  is the back and forth frequency of the reptating polymer chain. This was predicted by de Gennes on the basis of scaling arguments. In order to compare our results with the crossing density of the PT model, the temperature dependence of  $\sigma(\tau)/\sigma(\infty)$  can be modeled by taking into account the following Arrhenius relation for the linear diffusion coefficient (back and forth frequency):

$$\nu = \nu_0 \exp(-\Delta E/kT) \quad (2)$$

Here  $\Delta E$  is defined as the activation energy for the back and forth motion and  $k$  is the Boltzman constant. Combining eqs. 1 and 2, a useful relation is obtained as

$$\sigma(T)/\sigma(\infty) = R \exp(-\Delta E/2kT) \quad (3)$$

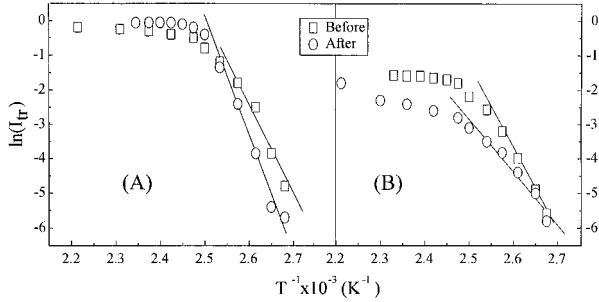
where  $R = (8 \nu_0 t/(N^2))^{1/2}$  is a temperature-independent coefficient.

The increase in  $I_{tr}$  is already related to the disappearance of particle–particle interfaces, i.e., 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 phenomenological equation can be written as

$$I_{tr}(T)/I_{tr}(\infty) = R \exp(-\Delta E/2kT) \quad (4)$$

Logarithmic plots of  $I_{tr}$  versus  $T^{-1}$  for the aged and nonaged samples are presented in Figure 4(A and B) for PVP and PVA films annealed for 10 min, respectively. The activation energies  $\Delta E$  for all samples are produced by fitting the data to the logarithmic form of eq. 4 and are listed in Table II for both the nonaged and aged samples.

These  $\Delta E$  values are large enough to be responsible for the translational motion of a polymer chain and can be attributed to the backbone motion. Similar activation energies were measured for deuterated and protonated polystyrene bilayers during welding by using secondary ion mass spectroscopy.<sup>29</sup>  $\Delta E$  values were produced using Arrhenius relation for the self-diffusion coefficient  $D$  and are found to be varied with the molecular weight such as 84.9, 64.2, 59.9, and 61.4 kcal mol<sup>-1</sup> for  $1.1 \times 10^5$ ,  $1.9 \times 10^5$ ,  $6.9 \times 10^5$ , and  $1.1 \times 10^6$  molecular weights, respectively. The SANS technique was also used to measure  $\Delta E$  values during film formation from deuterated and



**Figure 4** Logarithmic plot of  $I_{tr}$  data from Figures 1 and 2 versus inverse annealing temperature ( $T^{-1}$ ) for A-PVP and B-PVA for 10 min. Annealing times before and after aging. Data is fitted to eq. 4 to produce  $\Delta E$  values.

protonated polystyrene latex particles.<sup>31</sup> Films were annealed several times above  $T_g$  and center of mass diffusion coefficients were determined for  $1.5 \times 10^5$  and  $1.8 \times 10^5$  molecular weight samples. The activation energies for the above samples were obtained from the Arrhenius plots and are found to be 48 and 55 kcal mol<sup>-1</sup> respectively for the temperature range  $125 \leq T \leq 155^\circ\text{C}$ . It is observed that when the cosurfactant was used the activation energy dropped to 30 kcal mol<sup>-1</sup> for the  $1.5 \times 10^5$  sample.<sup>30</sup> These  $\Delta E$  values can be compared with the very early ones measured as 40 and 15 kcal mol<sup>-1</sup> for  $4.4 \times 10^4$  and  $2.4 \times 10^3$  mol weights at  $180^\circ\text{C}$  temperature.<sup>31,32</sup> All these works indicate that  $\Delta E$  values are strongly dependent on the treated temperature range and the molecular weight of the polymeric samples.

In this work the observed  $\Delta E$  values for each experimental set are found to be strongly dependent on the molecular weight of the PS

chains in each particle.  $\Delta E$  values were obtained for the films prepared with higher molecular weight PS stabilized by PVP of PS in particle cause high  $\Delta E$  values in both cases. In other words, PS chains need 150.5 and 110.2 kcal mol<sup>-1</sup> for interdiffusion to form the non-aged and aged PS particles, respectively. The lower molecular weight of PS chains stabilized with PVA use less energy to move their center of mass across the junction surface to form a similar films from both the nonaged and aged samples. However, we may conclude that delay in the film formation and bad quality of the forming films of the aged particles most probably was caused by lower motion of the higher molecular weight PS chains, which need less energy at higher temperature region to execute their backbone motion. The nonaged samples required larger activation energies at low temperature region to execute their backbone motion. It should be noted that there is no correlation between the observed  $\Delta E$  values and the annealing time interval. There is a strong phase separation during film formation from the PVA particles, which results in highly scattered  $\Delta E$  values.

In conclusion, in this work we used a very simple method (UVV) and a model (PT) to calculate the backbone activation energies for interdiffusion polymer chains during film formation from aged and nonaged PS latexes. Here it is observed that PVP stabilizer forms more homogeneous PS films than do films prepared using the PVA stabilizers. This phenomenon was explained by considering average molecular weight of PS,  $T_g$  values of the stabilizers, and compatibility of PS with

**Table II** Experimentally Observed  $\Delta E$  Values in Various Time Intervals of Annealing for the Nonaged and Aged Samples<sup>a</sup>

Time Interval (min)	2.5	5.0	10.0	15.0	20.0	Average
PVA/nonaged ( $1.5 \times 10^4$ )	—	67.2	91.6	52.0	46.8	64.4
PVA/aged ( $2.2 \times 10^4$ )	55.4	51.2	58.1	—	—	54.9
PVP/nonaged ( $1.8 \times 10^4$ )	144.7	155.3	146.7	155.5	—	150.5
PVP/aged ( $2.9 \times 10^4$ )	100.6	117.2	112.7	—	—	110.2

<sup>a</sup>  $\Delta E$  values were found by fitting the  $I_{tr}$  data to eq. (4). Energy units are in kcal/mol. The last column gives the average  $\Delta E$  values. The molecular weight of polystyrene in each particle are given in the parentheses.

these polymeric stabilizers. Here we have to note that for very short annealing time intervals (2.5 and 5 min) the range of temperature slightly moves to higher values, even though the slopes produce similar  $\Delta E$  values with the samples annealed at longer time intervals (20, 15, and 10 min.) It is observed that aged PS latex particles form less transparent (bad quality) films than the nonaged latexes even when annealing them at higher temperatures.

## REFERENCES

1. Struik, L. C. E. *Physical Ageing in Amorphous Polymers and Other Materials*; Elsevier: Amsterdam, Holland, 1978.
2. Mohammadi, N.; Klein, A.; Sperling, L. H. *Macromolecules* 1993, 26, 1019.
3. Sambasivan, M.; Sperling L. H.; Klein, A. *Macromolecules* 1995, 28, 152.
4. Pekcan, Ö.; Arda E.; Kesenci, K.; Pişkin, E. *J Appl Polym Sci* 1257, 68, 1998.
5. Sambasivan, M.; Klein, A.; Sperling, L. H.. *J Appl Polym Sci* 1995, 58, 357.
6. Wang, Y.; Winnik, M. A. *J Phys Chem* 1993, 97, 2507.
7. Canpolat, M.; Pekcan, Ö. *Polymer* 1995, 36, 4433.
8. Canpolat, M.; Pekcan, Ö. *Polymer* 1995, 36, 2025.
9. Pekcan, Ö.; Canpolat, M.; *J Appl Polym Sci* 1996, 59, 1699.
10. Guerro, R. *Macromol Symp* 1990, 35, 389.
11. Voyutskii, S. S. *Autohesion and Adhesion of High Polymers*; Wiley: New York, 1963.
12. Gennes, P. G. *C R Acad Sci (Paris)* 1980, 291, 219.
13. Prager S.; Tirell, M. *J Chem Phys* 1981, 75, 5194.
14. Kim, Y. H.; Wool, R. P. *Macromolecules* 1983, 16, 115
15. Kim, K. D.; Sperling, L. H.; Klein, A. *Macromolecules* 1993, 26, 4624.
16. Pekcan, Ö.; Winnik, M. A.; Croucher, M. D. *Macromolecules* 1990, 23, 2673.
17. Wang, Y.; Zhao, C. L.; Winnik, M. A. *J Chem Phys* 1991, 95, 2143.
18. Wang, Y.; Winnik, M. A. *Macromolecules* 1993, 26, 1347.
19. Canpolat, M.; Pekcan, Ö. *J Polym Sci Polym Phys Ed* 1996, 34, 691.
20. Pekcan, Ö. *Trends Polym Polym Sci* 1994, 2, 236.
21. Pekcan, Ö.; Kemeroğlu, F.; Arda, E. *Eur Polym J* 1998, 34, 1371.
22. Pekcan, Ö.; Kemeroğlu, F. *J Appl Polym Sci* 1999, 72, 981.
23. Pekcan, Ö.; Arda, E. *J Appl Polym Sci.* (in press).
24. Tuncel, A.; Kahraman, R.; Pişkin, E. *J Appl Polym Sci* 1993, 50, 303.
25. Tuncel, A.; Kahraman, R.; Pişkin, E. *J Appl Polym Sci* 1993, 51, 1485.
26. Shen, S.; Sudol, E. D.; El-Aasser, M. S. *J Polym Sci Polym Chem* 1993, 31, 1393.
27. Shen, S.; Sudol, E. D.; El-Aasser, M. S. *J Polym Sci Polym Chem* 1994, 32, 1087.
28. Brandrup, J.; Immergut, E. H. *Polymer Handbook*, 3rd ed.; Wiley: New York, 1989.
29. Whitkow, S. W.; Wool, R. P. *Macromolecules* 1991, 24, 5926.
30. Kim, K. D.; Sperling, L. H.; Klein, A. *Macromolecules* 1994, 27, 6841.
31. Antonietti, M.; Coutandin, J.; Grutter, R.; Sillescu, H. *Macromolecules* 1984, 17, 798.
32. Bachus, R.; Kimmich, R. *Polymer* 1983, 24, 964.