PMMA concentration in the mixtures were discussed by comparing their surface pressures.

Acknowledgment. We thank Professor A. Takahashi for his encouragement. We also thank Dr. T. Shiibashi at Japan Synthetic Rubber Co. for NMR measurements. This work was supported in part by a Grant-in-Aid for Scientific Research by the Ministry of Education, Science and Culture (63550664).

References and Notes

(1) den Engelsen, D.; de Koning, B. *J. Chem. Soc., Faraday Trans. 1* **1974,** *70,* 1603 and 2100.
(2) Mics, S. *Electronanal. Chem. Interface Electrochem.* **1975,** *62,* 291.
(3) Benjamins, J.; De Feijter, J. A.; Evans, M. T. A.; Graham, D. E.; Phillips, M. C. *Discuss. Faraday Soc.* **1975,** *59,* 218.
(4) de Feijter, J. A.; Benjamins, J.; Veer, F. A. *Biopolymers* **1978,** *17,* 1759.
(5) Graham, D. E.; Phillips, M. C. *J. Colloid Interface Sci.* **1979,** *70,* 415.
(6) Kawaguchi, M.; Oohira, M.; Takahashi, A. *Polym. J.* **1980,** *12,* 849.
(7) Ducharme, D.; Salesse, C.; Leblanc, R. M. *Thin Solid Films* **1985,** *132,* 83.
(8) Ducharme, D.; Tessier, A.; Leblanc, R. M. *J. Chem. Phys.* **1987,** *58,* 571.
(9) Kawaguchi, M.; Tohyama, M.; Mutoh, Y.; Takahashi, A. *Langmuir* **1988,** *4,* 407.
(10) Kawaguchi, M.; Tohyama, M.; Takahashi, A. *Langmuir* **1988,** *4,* 411.
(11) Sauer, B. B.; Yu, H.; Kim, M. W. *Langmuir* **1989,** *5,* 278.
(12) Sauer, B. B.; Yu, H.; Yazdanian, M.; Zografi, G.; Kim, M. W. *Macromolecules* **1989,** *22,* 2332.
(13) Gabrielli, G.; Puggelli, M.; Faccioli, R. *J. Colloid Interface Sci.* **1971,** *37,* 213; **1973,** *44,* 177.
(14) Gabrielli, G.; Puggelli, M.; Ferroni, E. *J. Colloid Interface Sci.* **1974,** *47,* 145.
(15) Gabrielli, G.; Baglioni, P. *J. Colloid Interface Sci.* **1980,** *73,* 582.
(16) Gabrielli, G.; Puggelli, M.; Baglioni, P. *J. Colloid Interface Sci.* **1982,** *86,* 485.
(17) Kawaguchi, M.; Nishida, R. *Langmuir* **1990,** *6,* 492.
(18) Wu, S.; Huntsberger, J. *J. Colloid Interface Sci.* **1969,** *29,* 138.
(19) Kuzmenka, D.; Granick, S. *Macromolecules* **1988,** *21,* 779.
(20) Rennie, A. R.; Crawford, R. J.; Lee, E. M.; Thomas, R. K.; Crowley, T. L.; Roberts, S.; Qureshi, M. S.; Richards, R. W. *Macromolecules* **1989,** *22,* 3466.
(21) Goodrich, F. C. *Proc. Int. Congr. Surf. Act., 2nd* **1959,** *1,* 85.
(22) Gaines, G. L., Jr. *J. Colloid Interface Sci.* **1966,** *21,* 315.
(23) Martuscelli, E.; Pracella, M.; Wang, P. Y. *Polymer* **1984,** *25,* 1097.
(24) Archer, R. *J. Opt. Soc. Am.* **1962,** *52,* 970.
(25) Bootsma, G. A.; Meyer, F. *Surf. Sci.* **1969,** *14,* 52.
(26) *Polymer Handbook*; Brandrup, J., Immergut, E. H., Eds.; Wiley: New York, 1975.

Characterization of Film Formation from Polystyrene Latex Particles via SANS. 1. Moderate Molecular Weight

J. N. Yoo,[†,‡,§] L. H. Sperling,[*,†,‡,§,∥] C. J. Glinka,[⊥] and A. Klein[†,§]

Center for Polymer Science and Engineering, Materials Research Center, Department of Chemical Engineering, and Department of Materials Science and Engineering, Whitaker Laboratory No. 5, Lehigh University, Bethlehem, Pennsylvania 18015, and Institute for Materials Science and Engineering, National Institute of Standards and Technology, Gaithersburg, Maryland 20899

Received September 20, 1989; Revised Manuscript Received February 16, 1990

ABSTRACT: Deuterated and protonated polystyrene latexes of 275-Å radius and 250 000 g/mol were mixed together to give 6 mol % of deuterated polystyrene. After removal of the aqueous phase and surfactants, the dry latex particles were sintered to full density at 110 °C under a pressure of 9.0 MPa by using a vacuum hot press for 40 min. These sintered films were annealed at 144 °C from 5 min to 48 h. Small-angle neutron scattering, SANS, measurements were made to evaluate the interdiffusion through an apparent increase in size of the deuterated polystyrene-rich particles, while tensile strength measurements were carried out on the corresponding protonated samples. For the present system, the minimum depth of molecular diffusional penetration for full tensile strength (3.04×10^7 N/m^2) was found to be about 110–120 Å, comparable to the weight-average radius of gyration, R_g^w, of the whole polystyrene chain. An elbow in the tensile strength–penetration depth relationship was found at 45–50 Å, corresponding to the critical molecular weight for entanglement. After an apparent induction period, the tensile strength increased with time to the one-fourth power, as predicted by Wool et al. After 48 h of annealing at 144 °C, complete molecular mixing was achieved via interdiffusion of deuterated and protonated species.

Introduction

The process of film formation from a latex can be divided into three stages: (a) evaporation of water, (b) coalescence and deformation of latex particles, and (c) interdiffusion of polymer chains between adjacent particles. Extensive research has been devoted to the first and second stages of film formation, while the interdiffusion problem has received little attention because of instrumental limitations. The present experiments utilize small-angle neutron scattering (SANS) to determine the latex particle and polymer radii of gyration in the films as a function of annealing time, from which molecular interdiffusion can be evaluated and compared with tensile strength buildup.

---

[*] To whom correspondence should be sent.

[†] Center for Polymer Science and Engineering, Lehigh University.

[‡] Materials Research Center, Lehigh University.

[§] Department of Chemical Engineering, Lehigh University.

[∥] Department of Materials Science and Engineering, Lehigh University.

[⊥] National Institute of Standards and Technology.

0024-9297/90/2223-3962$02.50/0

Using the SANS technique, Linne et al.[1] investigated the early stages of polymer chain interdiffusion. A 380-Å-diameter polystyrene latex was synthesized by seeded emulsion polymerization, which contained 50 mol % deuterated polystyrene chains of 5.85 × 10^6 molecular weight. After removal of the aqueous phase and surfactants, the dried polystyrene particles were subject to mild molding under vacuum, just sufficient enough to form fully dense films. Molded samples were annealed at 160 °C for various times and then evaluated by SANS and an indentation toughness test.

Initially, the high molecular weight polystyrene chains were constrained in the latex particles with radii of gyration 4 times smaller than that in the relaxed state. On the basis of the rate of increase in the radius of gyration of the polystyrene single chains, Linne et al.[1] reported that initial interdiffusion was hindered, most likely caused by residual interfacial effects such as the presence of sulfate chain end groups. Preliminary indentation toughness test results suggested that the diffusion across the particle boundaries to a level of 50–60 Å, as evidenced by an increase in the radius of gyration, was sufficient enough to develop fully healed films of polystyrene.

Hahn et al.[2,3] carried out studies on interdiffusion during the course of film formation form *n*-butyl methacrylate based copolymer latexes. Deuterated and protonated latexes were mixed and then dried. The dried films were annealed at higher temperatures than the glass transition temperatures of the copolymers and followed by SANS measurements to estimate the apparent increase of the radius of gyration of the deuterated particles. They concluded that coalescence of copolymer latex particles was due to a massive interdiffusion of polymer chains between particles.

Film formation from latex particles and interface healing in the bulk polymers are analogous in terms of chain interdiffusion requirements. Jud et al.[4] reported that for full material strength the penetration depth of polymer chains was calculated to be between 20 and 30 Å in crack healing experiments with poly(methyl methacrylate), which is half the distance of the radius of gyration for PMMA of the critical molecular weight for entanglement.

Wool et al.[5,6] have extensively studied healing problems of polymer interfaces and developed the minor chain reptation model based on de Gennes' reptation model for a unidirectional diffusion system. One of their major conclusions was that mechanical strength buildup during interface healing should have a one-fourth power dependence on time. Kline and Wool[7] recently examined strength development during the course of welding of polystyrene surfaces using a lap shear joint method. On the basis of reptation dynamics, it was concluded that the time to achieve complete healing was of the same order of magnitude as the viscoelastic relaxation time, which was equal to the time required for a polymer chain to diffuse the distance of its root-mean-square end-to-end vector.

The purpose of the present paper is to examine the relationships among the fundamental polymer chain diffusion characteristics of the latex particles, the concomitant depth of interdiffusion during film formation from latex particles, and mechanical strength buildup.

Experimental Section

Polymerization. Polystyrene latexes containing 100% deuterated species or 100% protonated species were prepared by bottle emulsion polymerization based on the recipe shown in Table I. The protonated styrene (Aldrich Co.) and the deuterated styrene (Cambridge Isotope Laboratories, 98%) were purified by removing the inhibitors through a neutral alumina packed column. A mixed surfactant system of sodium lauryl sulfate (anionic, Fisher Scientific) and Triton X-100 (nonionic, Rohm and Haas) was employed. Potassium persulfate was used as an initiator, potassium hydroxide as a pH regulator, and carbon tetrachloride as a chain-transfer agent.

Table I
Polymerization Recipe of Polystyrene Latexes[a]

ingredients	parts by wt
water (deionized distilled)	324.0
styrene	16.0
potassium persulfate	0.9
KOH	0.135
sodium lauryl sulfate, SLS	0.54
Triton X-100	5.4
CCl_4	1.0

[a] Polymerization temperature, 60 °C; reaction time, 22 h.

Table II
Characterization of Polystyrene Latexes

sample	M_n	M_w	M_z	M_w/M_n	particle radii,[a] Å
deuterated polystyrene	69 000	250 000	562 000	3.6	275
protonated polystyrene	68 000	259 000	610 000	3.8	272

[a] Determined by photon correlation spectroscopy.

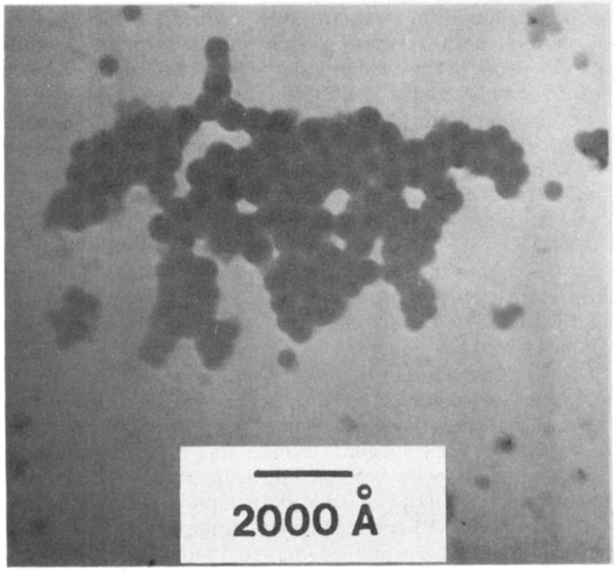

Figure 1. TEM picture for the deuterated polystyrene latex (magnification ×64 800).

Characterization. The molecular weight and molecular weight distributions were analyzed by gel permeation chromatography (Waters). Photon correlation spectroscopy (Coulter N4MD) was used to measure the particle size of the latexes in the aqueous dispersion; see Table II. Particle size and particle size distribution were determined by transmission electron microscopy (TEM, Philips 300). A particle size dispersity index of about 1.07 was obtained on the basis of the TEM picture shown in Figure 1. SANS measurement for the deuterated latex was made to determine the particle size excluding the surfactant layer (see the SANS Measurements section). For particle size determination, although the results of three techniques agreed considering the surfactant layer thickness in aqueous dispersion, the photon correlation spectroscopy was reported, because (1) more particles were counted and (2) the surfactants made the TEM boundaries somewhat indistinct. Within experimental error, the protonated and deuterated latexes are substantially identical in both molecular weight and size.

Sample Treatment and Sintering. The deuterated latex was mixed with 14.6 times its weight of the identical protonated polystyrene latex yielding 6 mol % of deuterated polystyrene. This composition was determined to ensure that each deuterated latex particle is surrounded by only protonated particles and to achieve a reasonable intensity to noise ratio in the SANS experiment. After the latex was dried at 40 °C for 2 days, the dried cake was extracted with excess methanol for 3 days to remove the nonionic surfactant, Triton X-100. Hot distilled water extraction was employed to remove the anionic surfactant, sodium lauryl sulfate. The wet powder was dried in a vacuum oven at 60 °C for 24 h. Differential scanning calorimetry studies indicated that almost all of the surfactant was removed, since T_g increased from 69 to 107 °C (at a heating rate of 20 °C/min) as surfactant was removed. The dried polystyrene particles were sintered by using a vacuum hot press at 110 °C for 40 min under a pressure of 9.0 MPa. These conditions are just sufficient enough to form a void-free, fully dense film, while minimizing chain interdiffusion between neighboring particles.

Specimen Annealing. The resulting bulk films of about 0.8-mm thickness and 3.75-cm diameter were annealed at 144 °C for various times. To prevent sample distortion during the annealing process, the sample was placed within a steel O-ring spacer sandwiched between two thin steel plates. Binder clips were used to hold the assembly together. For each experiment, the sample was then placed in a forced convection oven and 30 min were allowed for temperature equilibrium before the clock was started to measure the annealing time. As soon as the samples were taken out of the oven, they were quenched in a 15 °C water bath to inhibit any further diffusion.

For the blank SANS samples and the tensile strength studies 100% protonated samples were prepared by the same procedures. The density of each sample was determined by flotation in aqueous NaCl solutions and found to average 1.061 ± 0.004 g/cm^3 for SANS samples (6 mol % deuterated polystyrene) and 1.058 ± 0.004 g/cm^3 for blank samples (100% protonated polystyrene). Since the nominal density of protonated polystyrene is 1.06 g/cm^3 and the theoretical density of 6 mol % deuterated polystyrene is estimated to be 1.064 g/cm^3, it was concluded that the present samples were fully dense.

SANS Measurements. The SANS measurements for the bulk films were made at the National Institute of Standards and Technology, with a two-dimensional position-sensitive detector (65 × 65 cm^2). Disk specimens with about 0.8 mm in thickness and 2.2 cm in diameter were used throughout the measurements. A neutron wavelength of 8.0 Å and a sample to detector distance of 3.6 m were used. A seven-beam converging collimation system[8] was employed to increase the illuminated sample area (and hence the scattered intensity). With this configuration, SANS data at scattering vectors between 0.0043 and 0.08 Å^{-1} were obtained. Calibration of the SANS instrument was done using a silica gel absolute intensity standard.

In order to measure the original size of the deuterated polystyrene latex particles excluding the surfactant layer, the SANS experiment for the deuterated latex was performed at the Los Alamos Neutron Scattering Center (LANSCE) by using their time-of-flight spectrometer.[9] The deuterated polystyrene latex sample was placed in a liquid-quartz cell having a 0.1-cm path length. A sample to detector distance of 4 m was employed. SANS data were collected over the range of scattering vectors $0.0037 < K < 0.1$ Å^{-1}.

The recorded intensities for the samples and blanks were radially averaged and converted to absolute values. The coherent intensities of the samples were obtained by subtracting the intensities of the corresponding blanks, which were composed of 100% protonated polystyrene.

Tensile Strength Test. Micro tensile strength studies were carried out on all protonated samples at room temperature by using an Instron universal testing machine. Dumbbell-type specimens were prepared by grinding the bulk films followed by rubbing the ground surface with fine sandpaper until smooth. A grip separation distance of 1.25 cm and a grip separation rate of 0.254 cm/min were employed.

Data Analysis

According to the Guinier approximation,[10] scattering from any isotropic substance in the low-angle region can be expressed by

$$\frac{\mathrm{d}\Sigma}{\mathrm{d}\Omega}(K) = \frac{\mathrm{d}\Sigma}{\mathrm{d}\Omega}(0)\exp(-K^2R_g^2/3) \qquad (1)$$

where $\mathrm{d}\Sigma/\mathrm{d}\Omega$ is the coherent scattering cross section per unit volume of the material. The quantitiy K is the wave vector and is equivalent to $(4\pi/\lambda)\sin(\theta/2)$, λ is the neutron wave length, θ is the angle of scatter, and R_g represents the radius of gyration of the isotropic substance. The quantity R_g can be obtained from the slope of the plot $\ln(\mathrm{d}\Sigma/\mathrm{d}\Omega)(K)$ vs K^2. For a sphere, radius R is related to the radius of gyration, R_g, by

$$R^2 = (5/3)R_g^2 \qquad (2)$$

Scattering from random polymer coils that follow Gaussian statistics can be represented by the Debye function[11]

$$\left[\frac{\mathrm{d}\Sigma}{\mathrm{d}\Omega}(K)\right]^{-1} = \frac{1}{C_NM_w}[P(K)]^{-1} \qquad (3)$$

where C_N is the sample optical constant given by

$$C_N = \frac{(a_H - a_D)^2N_A\rho(1-x)x}{M_D^2} \qquad (4)$$

and $P(K)$ is the single-chain form factor, a_H and a_D are the scattering lengths of protonated and deuterated structural units, respectively, in the polymer, N_A is Avogadro's number, ρ stands for the polymer density, x is the mole fraction of deuterated polymer, and M_D is the deuterated polymer molecular weight.

The Debye form factor for a random coil is given by

$$P(K) = \frac{2}{K^4R_g^4}[K^2R_g^2 - 1 + \exp(-K^2R_g^2)] \qquad (5)$$

In the Guinier region, where $K^2R_g^2 < 1$, an expansion of eq 3 yields

$$\left[\frac{\mathrm{d}\Sigma}{\mathrm{d}\Omega}(K)\right]^{-1} = \frac{1}{C_NM_w}\left(1 + \frac{K^2R_g^2}{3}\right) \qquad (6)$$

The R_g can be determined from the slope of the plot, $[(\mathrm{d}\Sigma/\mathrm{d}\Omega)(K)]^{-1}$ vs K^2, which is usually called the Zimm plot. In this case, R_g is the z-average radius of gyration.

Binder[12] derived an equation to obtain the diffusion coefficient, based on Cook's scattering equation[13] for spinodal decomposition of metal alloys. For the case of an ideal polymer solution, Binder's equation can be written as

$$I(K,t) = I(K,0)\exp(-2K^2Dt) + I(K,\infty)[1 - \exp(-2K^2Dt)] \qquad (7)$$

where $I(K,0)$ and $I(K,\infty)$ are the initial and equilibrium scattering intensities, respectively. D is the diffusion coefficient, and t stands for time.

Recently, Summerfield and Ullman[14,15] derived an equation to obtain the diffusion coefficient from SANS data on systems composed of randomly mixed clusters of protonated and deuterated polymers where Fick's law applies. They showed that $I(K,t)$, the SANS intensity at annealing time t, can be characterized by

$$I(K,t) = I(K,0)\exp(-2K^2Dt) + I(K,\infty)\left[1 - \alpha(0,t) - \frac{1-\beta}{1-\psi}\exp(-2K^2Dt)\right] \qquad (8)$$

where $\alpha(0,t)$ is the normalized integral of a radial correlation function, $\alpha(R,0)$, characterizing the initial

Table III
Summary of SANS and Tensile Strength Test Results of Polystyrene Latexes Based Films

annealing time	R_g,[a] Å	R, Å	av penetratn depth, Å	tensile strength, 10^6 N/m²	R_g^z,[b] Å	M_w[b]
dispersed latex	180	232				
sintered	224	289		41		
5 min	198	256	24	49		
15 min	207	268	36	149		
30 min	216	279	47	225		
1 h	241	311	79	249		
2 h	267	345	113	315		
4 h	280	360	128	328		
8 h	(171)			288	174	276 000
19 h	(156)			276	172	263 000
48 h	(143)			312	165[c]	252 000[c]

[a] Determined by the Guinier approximation. [b] Obtained by the Zimm plot. [c] Values corrected by using Ullman's tables[22] are R_g = 182 Å and M_w = 275 000.

configurations of the segregated clusters.

$$\Delta(0,t) = (8\pi Dt)^{-3/2}\int_0^\infty \alpha(R,0)\exp(-R^2/8DT)\,dR \quad (9)$$

where R is a radial position. Furthermore, β and ψ are defined by the relationship

$$\alpha(0,0) = \frac{\beta-\psi}{1-\psi} \quad (10)$$

where $\psi \le \beta \le 1$.

In the current SANS data, $I(K,\infty)$ is much smaller (less than 10%) than $I(K,0)$, especially in the low angles and short annealing times. Equations 7 and 8 are reduced to the same forms when the second term in eqs 7 and is neglected. On the basis of these equations, a diffusion coefficient can be determined from the slope of the plot, ln $[I(K,t)/I(K,0)]$ vs K^2t.

Results and Discussion

The radii of gyration of the particles were determined during the annealing process; see Table III. In the later stages of annealing, the data were better interpreted as small clusters of chains, and after 48 h of annealing interdiffusion was substantially complete, on the basis of the molecular weights. Equations 1 and 2 were used to evaluate the original size of the deuterated polystyrene latex particles and the apparent size of the deuterated polystyrene-rich particles. The size of the deuterated polystyrene-rich particles determined by this analysis is "apparent" because of the concentration gradient of the deuterated polystyrene at the diffusion front. The SANS data are compared to the tensile strength data in Table III.

The average depth of penetration of the polymer chains was obtained by subtracting the original radius of the deuterated polystyrene particles from the apparent radius of the deuterated polystyrene-rich particles measured by SANS during expansion; see Figure 2.

The apparent particle radius after sintering is much larger than the original size of the deuterated particles, attributed to the initial anisotropy of particles. This anisotropy is believed to disappear through physical relaxation on annealing,[16,17] since high pressure is not applied in the annealing process.

Figure 3 shows a typical Guinier plot, ln $(d\Sigma/d\Omega)(K)$ vs K^2. For relatively short annealing times, the single-chain scattering contribution to the total scattering intensity is negligible in the low-angle region.[18] However, as time increases, the single-chain scattering contribution cannot be neglected. In particular, the Guinier plots of the samples annealed for more than 4 h yielded apparent decrease particle sizes, which indicated that the deuterated particles, through chain diffusion, had started to diffuse into other deuterated particles, leaving decreasingly small clusters of deuterated chains. Hahn et al.[3] also observed the decrease in the size of the deuterated particles after a certain annealing time in similar experiments.

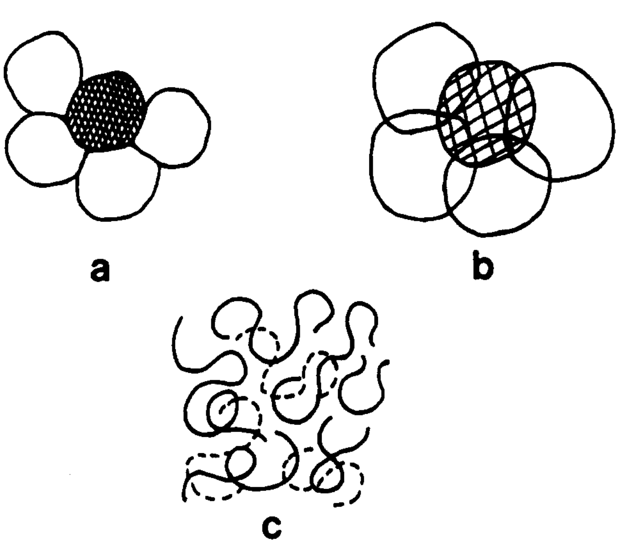

Figure 2. Interdiffusion from sintered latex particles as a function of annealing time: (a) fully dense films (deuterated particle cross-hatched); (b) mutual interdiffusion of particles (Deuterated particle appears to become enlarged.); (c) true deuterated (- - -)/protonated (—) polystyrene mutual solution.

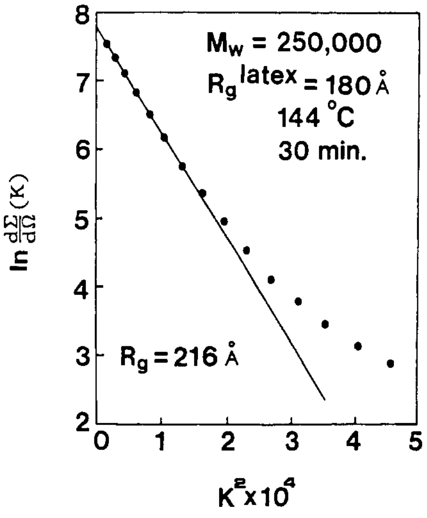

Figure 3. Determination of deuterated polystyrene particle radius of gyration via a Guinier plot.

On the basis of the above observations, Zimm plots were applied to the data for the samples annealed for more than 4 h to evalute the single-chain scattering behavior (see Figure 4). Zimm plots generally are linear when $KR_g < 1$. However, for the samples annealed for more than 4 h, there were a sufficient number of points falling on a straight line even above the Guinier region. This will be further discussed later.

The dependence of the average depth of penetration on the square root of time is illustrated in Figure 5. Since the linear relationship between the distance that a molecule travels and the square root of time is typical for diffusion processes, Figure 5 supports the validity of the current technique of measuring the average depth of penetration. The deviation of the last point from linearity can be

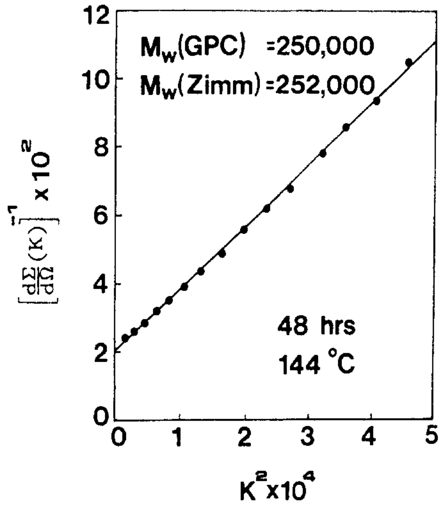

Figure 4. Determination of M_w and R_g^z of deuterated polystyrene via a Zimm plot.

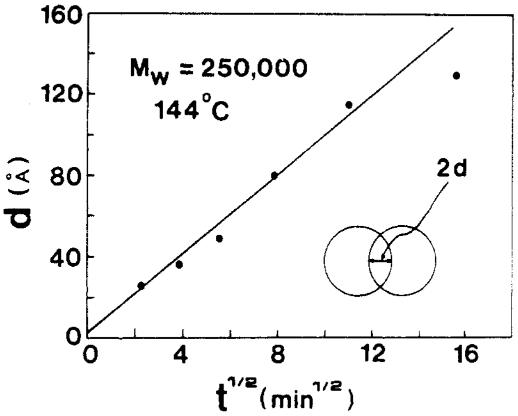

Figure 5. Interdiffusion penetration depth, d, of polystyrene latex chains during film formation.

interpreted as the result of the relatively high single-chain scattering contribution in obtaining the apparent particle size. By comparison of the measured SANS intensities with the calculated single-chain scattering intensities based on the Debye random-coil model, the single-chain scattering intensity amounted to 10–15% of the total intensity for the sample annealed for 4 h. Therefore, it seems to have a transient scattering behavior between the spherical scattering and single-chain scattering behavior.

Recently, Anderson and Jou[17,18] investigated the diffusion characteristics of polystyrene based on eq 8. The interdiffusion of annealed bulk films containing irregular clusters of 50 wt % deuterated and protonated polystyrene (prepared by anionic polymerization and then converted to a latex via direct emulsification) was characterized by SANS to determine the diffusion coefficient. In their analysis, the single-chain scattering term (second term in the right-hand side of eq 8) was neglected (which never amounted to more than 20% of $I(K,0)$ in the low-angle region). It was reported that the K-constant diffusion coefficients were between 9×10^{-16} and 1.2×10^{-15} cm^2/s and were obtained over the range $K = 0.004–0.007$ Å^{-1} for polystyrene of a monodisperse molecular weight of 68 000 at 130 °C.

For comparison purposes, the present SANS data were analyzed based on Binder's and Summerfield–Ullman's theory, as discussed in the Data Analysis section. The K-constant diffusion coefficients obtained by the above analysis were 4.0×10^{-16} and 2.9×10^{-16} cm^2/s at $K =$ 0.0055 and 0.0067, respectively, at 144 °C. These values were converted to those at Anderson and Jou's experimental conditions by using the relationships of $D \propto M^{-2}$ and the WLF equation[19] to give 2.4×10^{-16} and 1.8×10^{-16} cm^2/s, about 5 times smaller than the results of Anderson and Jou. In another experiment, using laminated polystyrene films, Stamm[20] obtained $D = 3.2 \times 10^{-15}$ cm^2/s, after similar conversion. The lower diffusion rate of the present system may be due to the presence of ionic end groups, such as sulfate groups, and/or the polydisperse nature in the molecular weight distribution of the present samples.

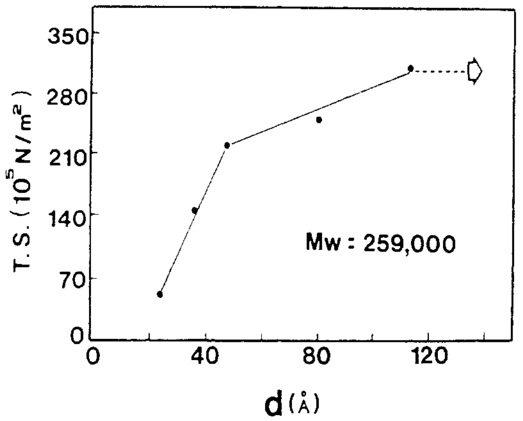

Figure 6. Tensile strength first increases and then levels off with increasing penetration depth.

As seen in Table III, the molecular weight determined from the Zimm plot is approaching the GPC molecular weight of the sample as the annealing time increases past 4 h. A theoretical z-average radius of gyration, R_g^z, in the bulk relaxed state[21] for such polystyrene single chains was calculated to be 206 Å for the present samples, somewhat larger than 165 Å, the measured R_g^z of the sample annealed for 48 h.

A large portion of the present data used in the Zimm plot analysis fall outside the true Guinier region ($0.7 < KR_g < 3.5$ in the present analysis). This problem was addressed by Ullman,[22] who discussed the corrections to M_w and R_g^z induced by exceeding the Guinier range and molecular weight polydispersity in Zimm plot analysis. From the molecular weight distribution data in Table II, Ullman's correction table, assuming the γ distribution of molecular weights, leads to about a 10% increase in M_w and about a 10% increase in R_g^z compared with the Zimm plot values. Because the corrections were small and uncertain, they were not applied to the present data, except after 48 h annealing; see Table III. Apparently, the experiment has run its course after 48 h, interdiffusion of protonated and deuterated species now yielding molecular weights and sizes straddling GPC and the corresponding theoretical value for R_g.

Figure 6 represents the tensile strength build-up feature as a function of the average depth of penetration. As seen in Figure 6, the rate of increase in tensile strength changes at the depth of penetration of about 45–50 Å, which is approximately the radius of gyration for polystyrene of the critical entanglement molecular weight, 32 000. A full tensile strength of 3.04×10^7 N/m^2 was built up at the average depth of penetration of about 110–120 Å. Interestingly enough, the theoretical weight-average radius of gyration, R_g^w, for polystyrene chains having M_w = 250 000 is 137 Å, based on the random-coil model. Therefore, the minimum depth of penetration for full strength seems to be comparable to the weight-average radius of gyration (The radius of gyration is a measure of

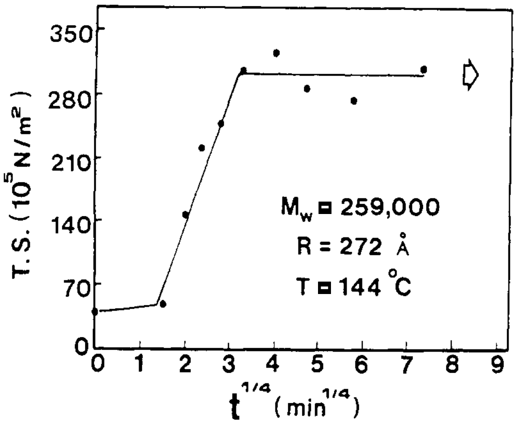

Figure 7. Wool plot, showing an apparent induction period, a portion following theory, and the film at full tensile strength.

half the distance across the chain. When a chain has diffused one R_g value across the interparticle boundary, it has about half its length on each side.) at least for the present system, suggesting that full tensile strength is achieved when the centers of mass of two chains diffusing out of neighboring particles pass each other.

Kline and Wool[7] reported that the time required for the complete welding of polystyrene of M_w = 262 000 in the lap shear joint experiment was one-fourth of the time required for a polymer chain to diffuse a distance equal to its chain end-to-end vector. When the linear relationship between the diffusion distance and the square root of time is used, assuming no induction period in interdiffusion, the minimum depth of penetration becomes half the end-to-end distance of the polymer chain, which is about 20% larger than the weight-average radius of gyration. Accordingly, within experimental error, the present result seems to be in fairly good agreement with their finding.

Wool et al.[5,6] showed that tensile strength buildup with interdiffusion should depend on time to the one-fourth power. A plot illustrating the present results is shown in Figure 7. Three regions of space are noted. There is an apparent induction period, followed by a portion that follows Wool's theory. Last, at long times, the tensile strength, fully developed, remains constant.

The delay time in the first region may have several explanations. For the present data, it may be an artifact derived from the initially strained nature of the polymer chains. However, the fractal nature of the mating polymer surfaces and/or the presence of ionic chain end groups are probable explanations here as well.

One last comment must be made on the shape of the sintered latex particles undergoing the actual diffusion process. In the hexagonal close-packed spherical model, a particle has 12 nearest neighbors. On sintering, the particle must form a dodecahedron, with more or less flat mating surfaces with its neighbors. In this case, Wool's theory for flat interfaces should work for relatively short distances of penetration to a good approximation.

Conclusions

Film formation from polystyrene latexes and compression molding generally are shown to be simple, quantifiable operations, the main features of molecular weight, temperature, and time all being interrelated increasingly by theory. Most interestingly, the interface healing theory of Wool et al. is shown to apply to film formation from the present polystyrene latex particles. Therefore, the reversible molecular motions of crack formation and healing, as explained by Wool et al., also take place during the interface healing and concomitant film formation.

At a penetration depth of about 110–120 Å, comparable to the weight-average radius of gyration of the whole polystyrene chain, a maximum tensile strength of 3.04 × 10^7 N/m^2 was achieved for the present system. The increase of tensile strength with penetration depth has an elbow around 45–50 Å, corresponding to the radius of gyration of the polystyrene chain of critical entanglement molecular weight. After an apparent induction period, the tensile strength increases with time to the one-fourth power, as predicted by Wool et al. After 48 h of annealing time at 144 °C, interdiffusion of the deuterated and protonated species was substantially complete.

Acknowledgment. We thank the National Science Foundation for support through Grant No. CBT-8820705. The SANS experiments were performed at the National Institute of Standards and Technology (formerly NBS) and Los Alamos Neutron Scattering Center (LANSCE). We thank Dr. Philip A. Seeger and Dr. Rex P. Hjelm, Jr., for their many helpful discussions and assistance with the SANS experiment at LANSCE.

References and Notes

(1) Linne, M. A.; Klein, A.; Miller, G. A.; Sperling, L. H. *J. Macromol. Sci., Phys.* **1988**, *B27* (2 and 3), 217.

(2) Hahn, K.; Ley, G.; Schuller, H.; Oberthür, R. *Colloid Polym. Sci.* **1986**, *264*, 1092.

(3) Hahn, K.; Ley, G.; Oberthür, R. *Colloid Polym. Sci.* **1988**, *266*, 631.

(4) Jud, K.; Kausch, H. H.; Williams, J. G. *J. Mater. Sci.* **1981**, *16*, 204.

(5) Wool, R. P.; O'Connor, K. M. *J. Appl. Phys.* **1981**, *52*, 5194.

(6) Kim, Y. H.; Wool, R. P. *Macromolecules* **1983**, *16*, 1115.

(7) Kline, D. B.; Wool, R. P. *Polym. Eng. Sci.* **1988**, *28* (1), 52.

(8) Glinka, C. J.; Rowe, J. M.; LaRock, J. G. *J. Appl. Crystallogr.* **1986**, *19*, 427.

(9) Hjelm, R. P. *J. Appl. Crystallogr.* **1988**, *21*, 618.

(10) Guinier, A.; Fournet, G. *Small Angle Scattering of X-rays*; John Wiley & Sons: New York, 1955.

(11) Debye, P. *J. Phys. Colloid Chem.* **1947**, *51*, 18.

(12) Binder, K. *J. Chem. Phys.* **1983**, *79*, 6387.

(13) Cook, H. *Acta Metall.* **1970**, *18*, 297.

(14) Summerfield, G. C.; Ullman, R. *Macromolecules* **1987**, *20*, 401.

(15) Summerfield, G. C.; Ullman, R. *Macromolecules* **1988**, *21*, 2643.

(16) Kramer, E. J.; Green, P. F.; Palmstrom, C. *Polymer* **1984**, *25*, 473.

(17) Jou, J. H. Ph.D. Dissertation, The University of Michigan, 1986.

(18) Anderson, J. E.; Jou, J. H. *Macromolecules* **1987**, *20*, 1544.

(19) Green, P. F.; Kramer, E. J. *Macromolecules* **1986**, *19*, 1108.

(20) Stamm, M. *Polym. Prepr.* **1987**, *28* (2), 56.

(21) Cotton, J. P.; Decker, D.; Benoit, H.; Farnoux, B.; Higgins, J. S.; Jannink, G.; Ober, R.; Picot, C.; des Cloizeaux, J. *Macromolecules* **1974**, *7*, 863.

(22) Ullman, R. *J. Polym. Sci., Polym. Phys. Ed.* **1985**, *23*, 1477.

Registry No. Polystyrene, 9003-53-6; perdeuterated polystyrene, 27732-42-9.