

A SANS STUDY OF SULFONATE END GROUP EFFECT ON POLYSTYRENE SELF-DIFFUSION

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Introduction

In the present study, polystyrene interdiffusion from miniemulsified latexes was investigated using small-angle neutron scattering (SANS), to examine the effect of sulfonate end-groups located at the water/polymer latex interfaces. Emphasis was placed on interdiffusion at short-times, in the $t^{1/4}$ regime.

The influence of polymer chain end-groups on interdiffusion is of special interest due to the differences in their behavior compared to the central portions of the chain.¹ According to reptation theory, polymer chain ends play a significant role in polymer diffusion processes because they lead the main chain out of their virtual tubes. In industrial practice, polymer chain ends may have various chemical structures depending on the use of initiators, chain transfer agents, or other special chemistries.

Yoo and coworkers^{2,3} and Kim and coworkers⁴ investigated latex film formation by SANS methods to understand the interdiffusion process. They measured diffusion coefficients in both anionically polymerized and free-radical polymerized polystyrene. The diffusion coefficients of latex films from conventional emulsion systems^{2,3} were an order of magnitude slower than those observed in the anionic miniemulsification system. The apparent slow interdiffusion in the conventional system was attributed to sulfate end-group aggregation and/or to a broad molecular weight distribution where the shortest chains interdiffused before measurements began.

Interdiffusion at short-times is of special interest because most changes in crack healing processes, molding, and latex film formation all occur during this time regime. For example, the mechanical strength in a latex film approaches its maximum when the interdiffusion distance is equal to about radius of gyration, typically less than a few tens of nanometers for most commercial polymers.^{2,4} Confirming theory,⁵ experimental data has shown that at short-times, the strength of interfaces depends upon annealing time to the one-fourth power during crack healing, polymer welding, and latex film formation.⁴

Experimental

Materials.⁶ Three types of polystyrene with narrow molecular weight distributions were synthesized via anionic polymerization (Polymer Source, Inc.). Purified styrene was added to an initiator solution of secondary butyl lithium in tetrahydrofuran (THF) at -78°C and the polymerization reaction was terminated by adding a few drops of methanol to make polystyrene with hydrogen end groups. Polystyrene with one sulfonic acid end group was initiated and propagated by the same method as the H-ended polystyrene and then terminated by adding 1,3-propane sulfone. Polystyrene with two sulfonic acid groups was synthesized by using a bifunctional initiator of sodium naphthalene and 1,3-propane sulfone as the terminator. The sulfonic acid functionality of the one-ended and two-ended polystyrene was determined by two-phase titration with Hyamine[®] 1622 (Fluka) in water-chloroform using methylene blue as indicator.⁷ Note that this synthesis produces *sulfonate* end groups rather than the commonly encountered *sulfate* end groups.

Latex Preparation. An artificial miniemulsification⁸ process was used to prepare latexes with uniform particle size. A deuterium-labeled latex was mixed with an proton-labeled latex.

Sintering and Film Annealing. A dried latex mixture was pressed at 10 MPa at a temperature between 100 and 110 $^{\circ}\text{C}$ for 30 min to one h to prepare a transparent film. Samples were then annealed at 125 - 145 $^{\circ}\text{C}$. All times reported are times in the mold and are ± 2 min due to thermal lag of heating. The temperatures reported all range $\pm 1.0^{\circ}\text{C}$.

SANS Measurements. The wavelength of the incident beam was monochromatized to 20 \AA by a velocity selector. The observed scattering intensity was corrected for electronic noise, background radiation and detector

inhomogeneity. It was normalized against a polymer standard to give the absolute intensity. Finally, it was circularly averaged to obtain the scattering intensity as a function of wave vector, Q . SANS data were collected over the range of scattering vectors $0.004/\text{\AA}^{-1} \leq Q \leq 0.039/\text{\AA}^{-1}$. Data were reduced and fits with standard deviations were calculated as described elsewhere.⁹ The standard deviations are given as error bars in the figures and as \pm values in the tables. In figures where the error bars were smaller than the plotted points, the bars were omitted for clarity. Since most of the data have $t^{1/4}$ time dependencies, the diffusion coefficients are apparent, non-Fickian in nature.

Results and Discussion

Interface Thickness by Porod Plot. An ideal two-phase system with sharp interfaces has been treated by Porod, who predicted a decrease in intensity proportional to Q^{-4} . The deviation of the scattering behavior from Porod's law of a two-phase system with finite interface thickness was treated by Koberstein et al.¹⁰

Figure 1 shows that the interface thickness of H-ended polystyrene is larger than that of one-SO₃-ended and two-SO₃-ended polystyrene. at a given time and annealing temperature, 125 $^{\circ}\text{C}$ and 145 $^{\circ}\text{C}$, indicating that the diffusion coefficients of polystyrene with one or two sulfonate end groups were lower than that of polystyrene with two H-ends.

Diffusion Coefficient Measurements by Guinier Plots. Guinier plots were prepared to determine the radius of gyration of the particles in annealed films, showing that the scattering intensity decreases at higher angles as annealing time increases. Based on the linear lines (Q range of $0.00421 \leq Q \leq 0.0082$) the radius of gyration were determined. Apparent diffusion coefficients were obtained by using the Fickian diffusion model.

$$R_g^2(t) = R_g^2(t_0) + 6D(t-t_0) \quad (1)$$

where D and t_0 are the diffusion coefficient and the reference time, respectively.

The average diffusion coefficients of polystyrene with one or two sulfonate end groups were five times and ten times lower, respectively, than that of polystyrene with two H-ends.

In order to investigate the temperature effect on interdiffusion, H-ended, one-sulfonate-ended, and two-sulfonate-ended polystyrene was annealed at 125 $^{\circ}\text{C}$, 135 $^{\circ}\text{C}$, and 145 $^{\circ}\text{C}$. In Figure 2, the activation energies for H-ended, one-sulfonate-ended, and two-sulfonate-ended polystyrene were obtained by using the Arrhenius equation. Activation energies for H-ended, one-sulfonate-ended, and two-sulfonate-ended polystyrene were 63 ± 2.5 , 68 ± 4.8 , and 71 ± 13 kcal/mol, respectively. Although the absolute values of diffusion coefficients for the three types of polystyrene are different, the activation energies are similar. These activation energies indicate that the same diffusion mechanism governs the diffusion process of the three types of polystyrene. According to the WLF equation, the diffusion coefficient is a function of free volume, which depends on the difference between annealing temperature and T_g . The difference in T_g of the three types of polystyrene are less than 0.5 $^{\circ}\text{C}$ by DSC, and identical within experimental error. The T_g data above combined with the activation energy data indicate that the sulfonate end groups do not change the diffusion mechanism, only changing the absolute values of diffusion coefficients.

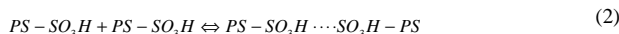
Aggregation. The polystyrene aggregate structure in the fully annealed state was investigated since the ionic end groups can induce an aggregation structure.

To investigate the polystyrene aggregate, various samples were prepared. Since a mixture of the same type of deuterated and protonated polystyrene can not show polystyrene aggregation, a mixture between polystyrene with sulfonate ends and polystyrene with H-end were prepared. If aggregation due to the end groups exists, the apparent molecular weight should become higher than observed with single molecules.

The apparent molecular weight and radius of gyration were determined on fully annealed samples by a Zimm plot. From the SANS spectra of fully annealed samples, the molecular weight and the radius of gyration of the chains and/or aggregates were determined. The sulfonate end groups of the samples were not neutralized, but used as received in the acid form. The mixture of deuterated and protonated polystyrene of the same end groups shows a molecular weight similar to GPC data with the quantity $R_g^2/M_w^{1/2}$ close to the reported value,¹¹ 0.275 (Table 1). However, the mixture of different types produced higher molecular weights. Deuterated one-SO₃-ended polystyrene in protonated

H-ended polystyrene has molecular weight 1.5 times higher than that in the same type polystyrene. Deuterated two-SO₃-end polystyrene in protonated H-end polystyrene has an even higher molecular weight, 5.8 times, while maintaining a value of $R_g^2/M_w^{1/2}$ within statistical error of 0.275, the single chain value.

The hydrogen bond between sulfonate groups might be the origin of the aggregate since the sulfonate groups is not neutralized. The equilibrium constant and H-bond energy can be estimated based by the following equation and the SANS data.



$$\begin{aligned} \Delta G &= -RT \ln K_{eq} \\ &= -RT \ln \left(\frac{[PS - SO_3H \cdots SO_3H - PS]}{[PS - SO_3H]^2} \right) \end{aligned} \quad (3)$$

where ΔG and K_{eq} represent the Gibbs free energy and the equilibrium constant between polystyrene and its dimer, respectively.

The concentration of sulfonate end groups and the average number of aggregates of deuterated one-sulfonate-ended polystyrene and protonated H-ended polystyrene were known, resulting in $\Delta G = -8.0$ kcal/mol which is in the order of one or two hydrogen bonds. For the mixture of deuterated two-sulfonate ended polystyrene and protonated H-ended polystyrene, ΔG was found to be -7.5 kcal/mol, substantially identical to that of one-sulfonate ended polystyrene case.

In a recent paper, Kim, et al.¹² showed that *sulfate* end groups located at the surface of latexes can speed very short time diffusion up. Thus, there is probably balance between aggregation and the head-start of polymer chain ends on the surface.

Conclusions

Film formation from a latex involves interdiffusion of the polymer chains. The interdiffusion behavior of polystyrene with H-ends, one sulfonate-end, and two sulfonate-ends are compared *via* small-angle neutron scattering (SANS) at short times. High molecular weight anionically synthesized polystyrenes were confined in latex particles utilizing an artificial miniemulsification technique. Interdiffusion of the polystyrenes in a latex film was carried out at temperatures of 125 – 145 °C. The diffusion coefficients of polystyrene with one or two sulfonate end groups were five times and ten times lower, respectively, than that of polystyrene with two H-ends.

The probable cause is end-to-end aggregation of the chains, supported by the ratio of $R_g^2/M_w^{1/2}$ remaining substantially constant.

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Table 1. The Apparent Molecular Weight and Radius of Gyration of Fully Annealed Samples. Samples consist of 6% deuterated and 94% protonated polystyrene.

Designation	Deuterated / Protonated	M_w (g/mol)	R_g (Å)	$R_g^2/M_w^{0.5}$
d-H / h-H	H-ends/ H-ends	317,800	161 ± 5	0.285
d-P / h-P	one-SO ₃ -end/ one-SO ₃ -end	238,300	134 ± 3	0.275
d-P / h-H	one-SO ₃ -end / H-ends	350,500	163 ± 3	0.275
d-S / h-S	two-SO ₃ -ends / two-SO ₃ -ends	247,500	139 ± 2	0.280
d-S / h-H	two-SO ₃ -ends / H-ends	1,447,500	331 ± 23	0.271

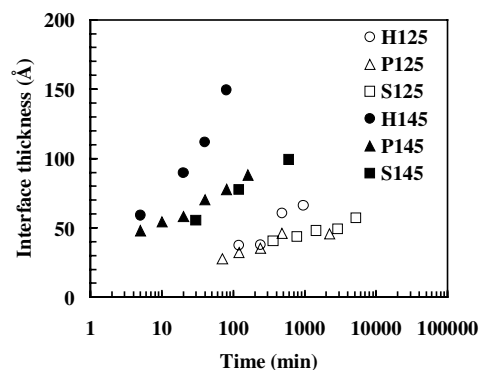


Figure 1. The interface thickness via the Porod plots of H-ended (circles, H125, H145), one-SO₃-ended (triangles, P125, P145), and two-SO₃-ended polystyrene (rectangles, S125, S145). Numbers (125 and 145) represent the annealing temperature (°C)

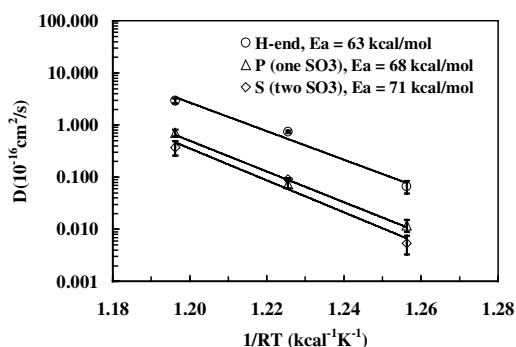


Figure 2. Arrhenius plots to determine the activation energies of polystyrene with H-ends (circles), one-sulfonate-end (triangles), and two-sulfonate-ends (diamonds).

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