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

Center for Polymer Science and Engineering, Lehigh University, Bethlehem, PA 18015-3194
*Rohm and Haas Company, 727 Norristown Rd, Spring House, PA 19477,
**Polymer Division, National Institute of Standards and Technology, Gaithersburg, MD 20899

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. 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 and Kim and coworkers 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 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 effects.

The maximum when the interdiffusion distance is equal to about the radius of gyration, $R_g$, represents the end-group effect on interdiffusion, which is significant for polymer diffusion processes because they influence 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.

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.

Figure 1 shows that the interface thickness of H-ended polystyrene is larger than that of one-SO$_3$-ended and two-SO$_3$-ended polystyrene. At a given time and annealing temperature, 125°C and 145°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 ≤ $Q$ ≤ 0.0082) the radius of gyration were determined. Apparent diffusion coefficients were obtained using the Fickian diffusion model:

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

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°C, 135°C, and 145°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. The average diffusion coefficients of polystyrene with one or two sulfonate end groups 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 the annealing temperature and $T_g$. The difference in $T_g$ of the three types of polystyrene is less than 0.5°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 $R_g^2/IM$ close to the reported value, 13.0 ± 0.275 (Table 1). However, the mixture of different types produced higher molecular weights. Deuterated one-SO$_3$-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 $R_g/M^{1/2}$ 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.

$$\Delta G = -RT \ln K_{eq}$$

$$\Delta G = -RT \ln \frac{[PS-SO_3 H \cdots SO_3 H \cdots PS]}{[PS-SO_3 H]} \quad (3)$$

where $\Delta G$ 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, $\Delta G$ 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. showed that sulfonate 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 $R_g/M^{1/2}$ remaining substantially constant.

**Acknowledgement.** The authors would like to acknowledge financial support through National Science Foundation Grant No. CTS-9810703.

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

<table>
<thead>
<tr>
<th>Designation</th>
<th>Deuterated / Protonated</th>
<th>$M_e$ (g/mol)</th>
<th>$R_g$ (Å)</th>
<th>$R_g/M_e^{1/2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>d-H / h-H</td>
<td>H-ends</td>
<td>317,800</td>
<td>161 ± 5</td>
<td>0.285</td>
</tr>
<tr>
<td></td>
<td>H-ends</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>d-P / h-P</td>
<td>one-SO3-end/one-SO3-end</td>
<td>238,300</td>
<td>134 ± 3</td>
<td>0.275</td>
</tr>
<tr>
<td></td>
<td>one-SO3-end/one-SO3-end</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>d-P / h-H</td>
<td>one-SO3-end/one-SO3-end</td>
<td>350,500</td>
<td>163 ± 3</td>
<td>0.275</td>
</tr>
<tr>
<td>d-S / h-S</td>
<td>two-SO3-ends/two-SO3-ends</td>
<td>247,500</td>
<td>139 ± 2</td>
<td>0.280</td>
</tr>
<tr>
<td></td>
<td>two-SO3-ends/two-SO3-ends</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>d-S / h-H</td>
<td>two-SO3-ends/two-SO3-ends</td>
<td>1,447,500</td>
<td>331 ± 23</td>
<td>0.271</td>
</tr>
<tr>
<td>d-S / h-H</td>
<td>two-SO3-ends/two-SO3-ends</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**References**

(6) Certain commercial materials and equipment are identified in this paper in order to specify adequately the experimental procedure. In no case does such identification imply recommendation by the National Institute of Standards and Technology nor does it imply that the material or equipment identified is necessarily the best available for this purpose.
(9) NG3 and NG7 30-meter SANS Instruments Data Acquisition Manual, 1996, National Institute of Standards and Technology Cold Neutron Research Facility.