

# A DIRECT COMPARISON OF SANS AND DET FOR POLYMER DIFFUSION DURING POLYSTYRENE LATEX FILM FORMATION

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## Introduction

Polymer diffusion at interfaces forms the basis for understanding the processes of mixing and homogenization of macromolecules. It has a wide range of applications such as adhesion and welding between polymeric materials, crack healing and polymer blending, and film formation from latexes. Among the various model systems, latex film formation was used for the interdiffusion study of polymer chains. Latexes are typically composed of small particles, of the order of tens to hundreds nanometers in diameter, and having a very large interface area per volume. Small-angle neutron scattering (SANS)<sup>1,2</sup> and direct nonradiative energy transfer (DET, a fluorescence spectroscopy) technique<sup>3,4,5</sup> were used in the last decade to measure the diffusion coefficients in latex film.

SANS and DET techniques on latex films rely on the same mathematical model to obtain diffusion coefficients in latex films. Both models use Fickian diffusion. Although both methods rely on the same mathematics, the diffusion coefficients from different methods are not guaranteed to have the same values due to the difference in measurement detail between the two methods. SANS measures apparent increases in the radius of gyration of the latex particles as a function of annealing time, while DET measures the fraction of mixing via diffusion between neighboring particles. Since the two methods measure different properties of latex particles to determine the diffusion coefficient, there arises the possibility that diffusion coefficients from the two methods can be different.

The present study aims at comparing the two methods directly. Of interest is the difference in measurement and analysis itself rather than in the sample labeling process. Various polystyrene samples were made for both SANS and DET at the same time. The samples were labeled with both deuterium and fluorescent groups to be used in both methods. Samples were composed of mixtures of two different latex particles. A mass fraction of 6 % latex particles was made from deuterated polystyrene with a mass fraction of 1 % fluorescent donor. The other 94 % of latex particles were made from protonated polystyrene with 1 % fluorescent acceptor.

## Experimental

**Materials.** For the DET experiment, monomers containing a fluorescent group were synthesized. 9-anthryl methacrylate (ANMA) was synthesized by reaction of methacryloyl chloride and 9-anthrone in base. 1-naphthylethyl methacrylate (NEMA) was prepared by reaction of methacryloyl chloride and 1-naphthylethanol.

**Polymerization.** Polystyrene, poly(styrene-*stat*-ANMA), and poly(styrene-*stat*-NEMA) with a relatively narrow molecular weight distribution were synthesized via a stable free radical process<sup>6</sup>. The two polystyrene samples are shown in Table 1. The deuterated polystyrene is labeled with NEMA fluorescence monomer to perform both SANS and DET experiment.

**Latex Preparation.** An artificial miniemulsification<sup>7</sup> process was used to prepare latexes with uniform particle size. A fluorescent donor-labeled latex was mixed with an acceptor-labeled latex.

**Sintering and Film Annealing.** A dried latex mixture was pressed at 10 MPa at a temperature between (100 and 110) °C for 30 min to one h to prepare a transparent film. Samples were then annealed at 120 °C. All times reported are times in the mold and are  $\pm 2$  min due to thermal lag of heating. The temperatures reported all range  $\pm 1.0$  °C based on previous studies.

**DET Measurements.** A pulsed hydrogen flashlamp selectively excites the naphthalene fluorophore at 280 nm. The emission is detected at 340 nm, via a photomultiplier tube operating in a time-correlated-single-photon-counting mode. The raw data are first deconvoluted from the instrument

response function, which typically has a (2 to 4) ns width at half height. Many functions could be applied to an analysis of the decay curve, however, a double exponential function built into the instrument software was used which produced reasonable  $\chi^2$  values ( $\leq 1.5$ ). As annealing time is increased, interdiffusion increases, and hence energy transfer also increases. The total number of radiative photons was calculated after the decay curves were fit to a double exponential function and integrated. Finally, the fraction of mixing,  $F_m$ , and diffusion coefficients were obtained.

**SANS Measurements.** The wavelength of the incident beam was monochromatized to 20 Å 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  $0.004/\text{Å}^{-1} \leq Q \leq 0.039/\text{Å}^{-1}$ . Data were reduced and fits with standard deviations were calculated as described elsewhere<sup>9</sup>. The standard deviations are given as error bars in the figures and as  $\pm$  values in the tables.

Table 1. Polystyrene Samples for DET and SANS.

Sample	$M_n$ (PDI) g/mol	Fluorescence Labeling, mass fraction	Deuteration
83A1	72000 (1.3)	Acceptor ANMA 1 %	none
DPS75K N1	75000 (1.3)	Donor NEMA 1 %	Deuterated styrene monomer (Cambridge Isotope Laboratories, 98%) <sup>8</sup>

## Results and Discussion

**SANS Results.** Guinier plots were prepared to determine the radius of gyration of the particles in the latex film. 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.

Porod plots were used to determine the interfacial thickness between protonated particles and deuterated particles. A Gaussian shape was used to describe the interface thickness. As a demonstration, Figure 1 shows a rough method of measuring the interface thickness without considering any background effect from the mixed region. The slope in Figure 1 indicates that the interface thickness increases with annealing time. The slope of the sample,  $33 \text{ Å}^2$ , for zero annealing time was zero within experimental error  $\pm 83 \text{ Å}^2$ , indicating that the interface of sintered sample was very sharp. A nonlinear fitting routine was used to fit this scattering along with background scattering from the mixed region and is shown in Table 2. The interfacial thickness also shows that the molecular interdiffusion between particles occurred from the very beginning of the annealing process.

The scaling law of time dependence of interface thickness obtained by Porod analysis of SANS data is plotted in Figure 2. The break point in  $\log(\text{time})$  v.s.  $\log(\text{interface thickness})$  was found at 20 min and 40 Å. The slope in Figure 2 is 0.21 at short annealing times and changes to 0.55 at longer annealing times. The reptation theory predicts that the slope should be 0.25 before the relaxation time and 0.5 after the relaxation time. Within experimental error, the slopes in Figure 2 conform to the theory.

**Direct Nonradiative Energy Transfer (DET).** Figure 3 shows the fraction of mixing and the apparent diffusion coefficients of latex films. The fraction of mixing at time zero and infinite time were chosen as zero and one, assuming that there was no interdiffusion in the sintered film. Since DET measured only the molecular mixing and was not influenced by physical relaxation of deformed particles, the fraction of mixing monotonically increased with longer annealing time of a donor particle.

There are many quantities in addition to diffusion coefficients that can be extracted from  $F_m$  data of DET measurement. At given  $F_m$ , a concentration profile in space can be constructed by using the initial particle size and the spherical Fickian model. Any information related to the diffusion process can

be obtained from the concentration profile. Table 2 shows calculations of radius of gyration and interface thickness. The quantities  $R_g$ , average diffusion distance,  $X$ , show reasonable agreement with a relative difference of less than 20 % for the most of data. However, the DET data do not show any break point, as did the SANS data in Figure 2.

**Table 2. Calculation of the Radius of Gyration and Interface Thickness Based on the Fraction of Mixing,  $F_m$ , from DET with the Fickian Diffusion Model.**

Time (min)	$F_m$	$R_g$ (calc., DET)	$R_g$ (SANS)	$X^*$ (calc., DET)	Interface thickness (SANS)
5	0.0918	-	$276 \pm 0.6$	18.0	$30.2 \pm 3.1$
10	0.124	285	$284 \pm 1.0$	24.6	$35.0 \pm 3.2$
20	0.224	302	$299 \pm 1.6$	46.6	$40.2 \pm 3.5$
40	0.266	312	$321 \pm 1.1$	56.6	$60.8 \pm 1.6$
120	0.479	385	$373 \pm 1.2$	116.0	$107.8 \pm 1.2$

\* Average diffusion distance.

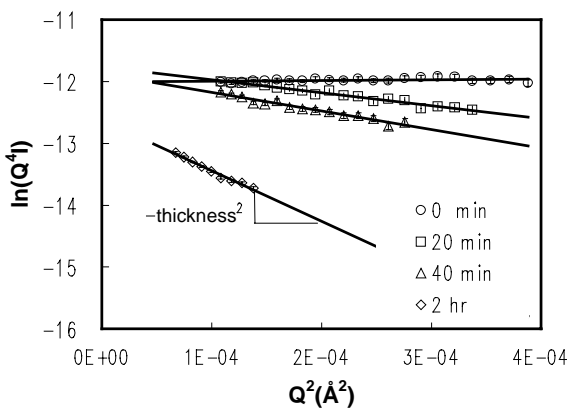
**Diffusion coefficients.** Table 3 compares the apparent diffusion coefficients obtained by SANS and DET. The diffusion coefficients from the two methods show agreement within a factor of two. Diffusion coefficients can be measured at short times with DET than with SANS, because particle deformation relaxation is not measured.

**Table 3. Apparent Diffusion Coefficients Obtained by SANS and DET.**

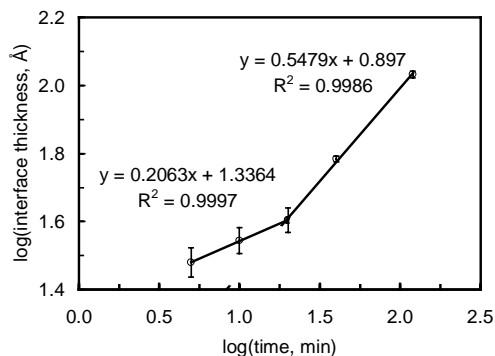
Annealing time (min)	$D(\text{\AA}^2/\text{s})$ , SANS	$D(\text{\AA}^2/\text{s})$ , DET
5	-	$1.46 \pm 0.72$
10	$2.54 \pm 1.44$	$1.28 \pm 0.42$
20	$2.49 \pm 0.70$	$2.20 \pm 0.16$
40	$2.12 \pm 0.20$	$1.42 \pm 0.21$
120	$1.51 \pm 0.04$	$1.65 \pm 0.25$

## Conclusions

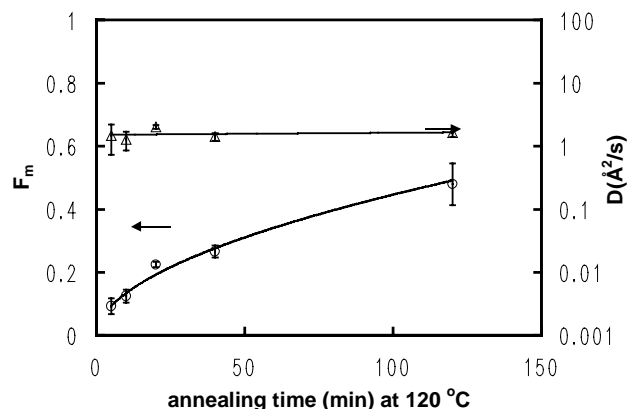
SANS and DET analysis were performed on exactly the same samples to remove any artifacts originating from sample differences. SANS and DET data provide various insights into the latex film formation process and mechanical strength development, especially in the very early time region. The interface shape in the sintered film was found to be sharp. The physical relaxation of deformed particles in sintered films was monitored by SANS while molecular interdiffusion was measured by DET without interference of physical relaxation. The diffusion coefficients obtained from SANS were slightly higher in most cases, within a factor of two than that determined by DET.



**Figure 1.** Porod plots were used to determine the interface thickness between deuterated particles and protonated particles. The slope is  $-(\text{thickness})^2$ .



**Figure 2.** The relationship between interface thickness and annealing time of SANS data at temperature = 120 °C.



**Figure 3.** The fraction of mixing (circle) and apparent diffusion coefficients (triangle) as functions of annealing times.

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