SMALL ANGLE NEUTRON SCATTERING (SANS) STUDIES OF DIFFUSION IN
BULK POLYSTYRENE NEAR THE GLASS TRANSITION TEMPERATURE (T_g)[*]

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Abstract - Ultraslow diffusion in bulk polymers has been measured by
SANS. The experiment begins by measuring scattering from heterogeneous
specimens containing domains of protonated-and deuterated-polymers at
temperatures far below T_g. The samples are subsequently held [annealed]
above T_g for a known time-interval, then cooled below T_g where SANS is
measured again. Scattering changes, from before to after annealing,
are analysed to obtain diffusion coefficients. The recent Summerfield -
Ullman procedure is used to deconvolute portions of the scattering
curve that decrease and increase with annealing time. Because of SANS
sensitivity to small distances, the method yields D $\approx 10^{-18}$ to 10^{-15}
cm^2/s after annealing times of 1-24 h.   Data analysis is complica-
ted by "smearing effects" which produce apparent Q-dependent diffusion
coefficients. Representative experimental results on polystyrene at
108°-130 ^{o}C are discussed.

INTRODUCTION

Scattering/diffusion experiments have been performed on binary metal
systems for many years   (Ref.1). The basic technique consists of forming a
heterogeneous, non-equilibrium specimen at low temperature where diffusion
is effectively zero. X-ray/neutron scattering from this specimen is
measured. The sample is then annealed, for a known period of time, at a
temperature where interdiffusion modifies the original segregated domains.
Finally, the sample is cooled and scattering is measured again. Diffusion
coefficients are computed from scattering changes with annealing time.
Scattering/diffusion methods provide independent measures of diffusion at
each scattering angle; for this reason they are uniquely able to explore
the presence or absence of Q-dependent diffusion.

Diffusion effects on scattering from binary metals is indicated
schematically below. Note that scattering effectively decays to zero for a
fully-annealed sample, where the two components are uniformly mixed.

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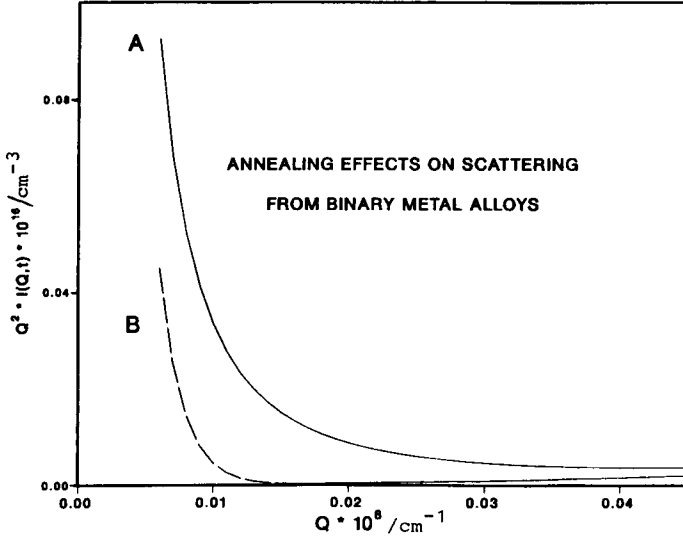   California 95120 USA

Fig. 1. Computer-simulation of SANS diffusion experiment for
a binary metal system. Curve (A) represents SANS from initial
specimen, plotted as $Q^2I(Q,0)$ versus Q. Curve (B) represents
a specimen annealed for intermediate time. Fully annealed
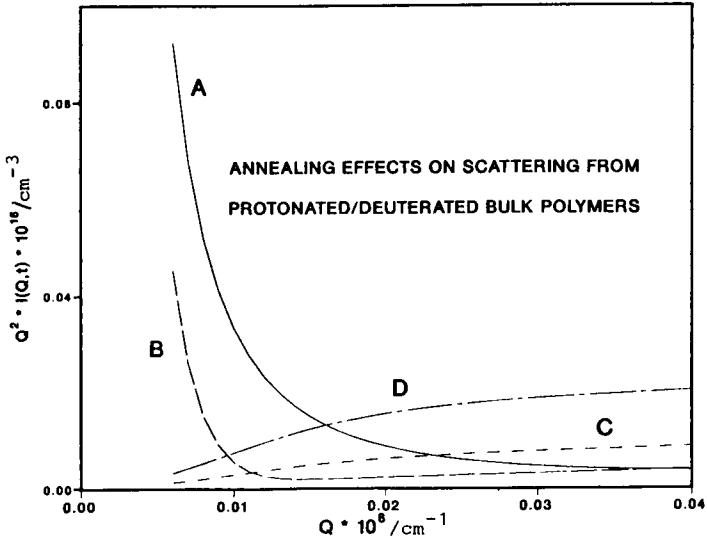specimens exhibit no appreciable scattering over this Q-range.

Fig. 2. Computer-simulation of SANS diffusion experiment for
a polymer system. Curve (A) represents SANS from initial
specimen, plotted as $Q^2I(Q,0)$ versus Q. Curves (B) and (C)
represent specimens annealed for intermediate times; Curve (D),
a fully annealed specimen.

Analogous diffusion experiments on protonated/deuterated polymers are complicated by the finite scattering of homogeneous samples. This difference results from the macromolecular and monomeric dimensions of polymers and metals, respectively. As a consequence of this, polymer SANS experiments typically exhibit [a] a low-Q portion that decreases with annealing time, and [b] a higher-Q portion that increases with annealing time.

Summerfield and Ullman (ref. 2) recently developed a method for deconvoluting decreasing and increasing portions of scattering/annealing curves. They showed that I(Q,t), the SANS after annealing time $\underline{t}$, can be expressed

$$I(Q,t) = I(Q,0) \exp\{ - 2DQ^2t\} + a(t) \ I(Q, \infty)$$

where I(Q,0) and I(Q,∞) are the scattering intensities from the initial and fully-annealed samples. The factor a(t), which increases to 1 as t → ∞, involves the integral of a space-correlation function. Decreasing and increasing parts of the scattering curve are not independent: They are related by the invariance of the integrated scattering intensity over all angles. One can obtain diffusion coefficients from either part of the scattering curve. In practice, it seems easier to use the decaying contribution since it is independent of the initial distribution of heterogeneities; i.e, independent of I(Q,0). On the other hand, analysing the increasing portion of the scattering curve requires information about I(Q,0) over all scattering angles, including angles below the experimental limit of SAXS and SANS instrumentation.

EXPERIMENTAL

Our experiments used 50:50 [wt %] protonated/deuterated polystyrene samples having matched molecular weights of 68000, 110000, 240000 and 600000. The heterogeneous specimens, formed by freeze-drying of latex suspensions, resembled a collection of spheres with a 900 nm average diameter. A detailed description of sample preparation appears elsewhere (ref. 3).

SANS measurements were carried out at the HFIR facility at Oak Ridge National Laboratory. The majority of the diffusion measurements was done at a sample-to-detector flight path of 16.5 m, a neutron wavelength of 4.75 x 10^{-8} cm and source/sample slits of 2.0 and 1.0 cm, respectively. Some preliminary experiments were performed at 6.89 m.

RESULTS

The Summerfield-Ullman analysis generated F(Q,t) = F(Q,0) exp{-2DQ²t} from raw experimental data. Plots of ln{F(Q,t)/F(Q,0)} versus (Q²t) were used to obtain the diffusion coefficients. Note that t and Q^2 are conjugate vari-ables in the case of simple diffusion. In order to optimize SANS beam-time, most of our experiments measured F(Q,t) at several Q-values and two annealing times. The intrinsic scatter from a small number of points produced a 50% uncertainty in diffusion coefficients (Table I).

More extensive measurements were performed on a specimen of 68000 MW polystrene at 130 °C: eleven different annealing times were used. We derived diffusion coefficients as

$$D_t = -0.5 \ \{dln[F(Q,t)/F(Q,0)]/d(Q^2)\}_t$$

from data at fixed annealing time $\underline{t}$ and variable Q, and as

$$D_Q = -0.5 \ \{d\ln[F(Q,t)/F(Q,0)]/dt\}_Q$$

from data at constant $\underline{Q}$ and variable $\underline{t}$. These values should be identical if D were independent of $\underline{Q}$ and $\underline{t}$. As shown below, we encountered systematic departures from predictions of simple diffusion theory indicating a 2X variation of D over the range $4 \times 10^5 < Q < 8.0 \times 10^5$ cm^{-1}.
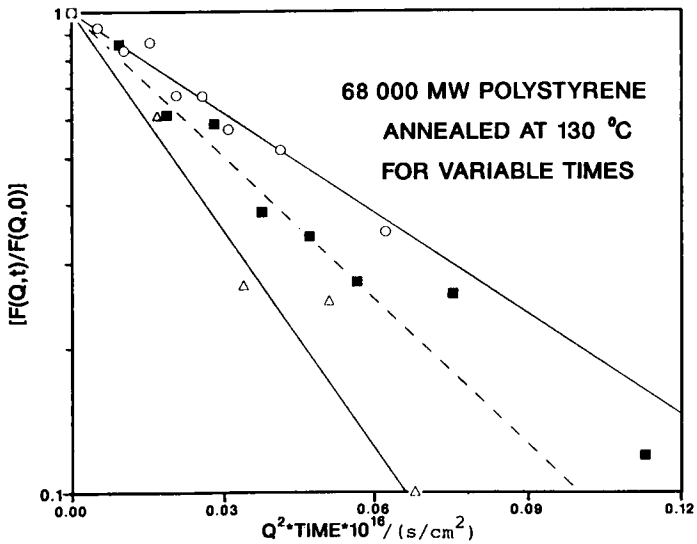

Fig. 3. Decay of experimental SANS with annealing time. Data, on 68000 MW polystyrene at 130 °C, were taken at fixed scattering angles and various times. Circles, Q = 4.15 x 10^5 cm^{-1}; squares, Q= 5.60 x 10^5 cm^{-1}; triangles, Q= 7.52 x 10^5 cm^{-1}.
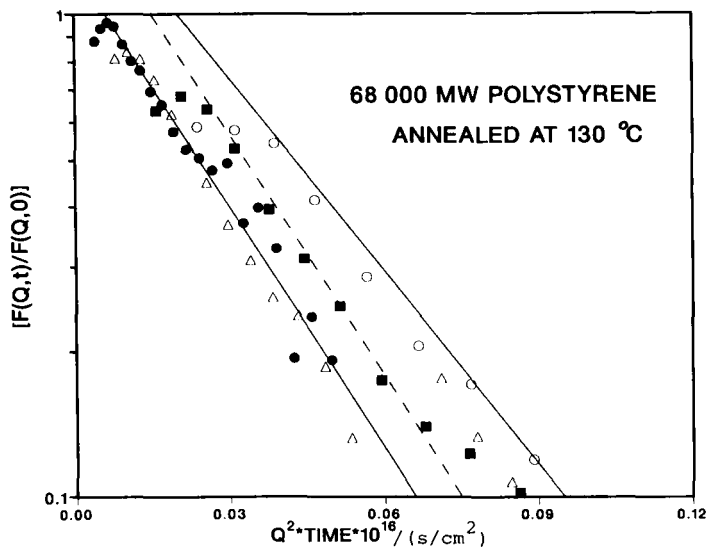
Fig. 4. Decay of experimental SANS with scattering angle (Q^2) at fixed annealing times. Filled circles, t = 300 s; triangles, t = 600 s; filled squares, t = 1200 s; open circles, t = 1800 s

Experimental SANS decreases abruptly with scattering angle. At low-Q, $I(Q,0)$ varies as Q^{-m} where m lies between 4 and 5, whereas at higher-Q, $I(Q,0)$ varies as Q^{-2}. This led us to examine possible slit-smearing effects on our data. Using instrumental parameters for the Oak Ridge facility, kindly supplied by Dr. G.D. Wignall, we calculated an instrumental broadening function of $\Delta Q_T = 2.1 \times 10^5$ cm^{-1} (ref. 3). This was used to simulate smearing effects at the detector [I_d] as:

$$I_d(Q_o,t) = \int I_s(Q,t) \exp\{-2.77((Q-Q_o)/\Delta Q_T)^2\} \, d(Q-Q_o)$$

I_s, the sample scattering intensity, was assumed to have the form

$$I_s(Q,t) = \{C_1 \, R_c^3 \, /(1+(QR_c)^2)^2\} \, \exp\{-2DQ^2t\},$$

where R_c is a correlation length. The coefficient C_1 is given by

$$C_1 = 8\pi\phi(1-\phi) \, (N_A\rho/M_M)^2 \, (a_H-a_D)^2,$$

where N_A is Avogadro's number, ϕ is the volume fraction deuterated polymer, ρ is the density, M_M is the monomer MW, and a_H, a_D are the neutron cross-sections for the C_8H_8 and C_8D_8 monomer units. Results of this simulation indicate that the apparent Q-dependence of experimental diffusion coeffi-

cients can be attributed to smearing effects. Additional experiments are
planned, using different instrumental geometries, to validate this. Note
that the experimental D-values shown in Table I are not corrected for
smearing effects.

TABLE I
SANS Diffusion Coefficients for 50:50
Protonated/deuterated Polystyrenes(HPS/DPS)

DPS-MW/HPS-MW [a)	T/$^{\circ}$C	D/(cm^2/s)
68000/68000	130	1.85 x 10^{-15}
	120	2.5 x 10^{-16}
	108	7.0 x 10^{-18}
110000/110000	130	1.1 x 10^{-15}
	120	1.6 x 10^{-16}
	108	1.8 x 10^{-18}
240000/233000	130	7.5 x 10^{-17}
	120	6.8 x 10^{-18}
697000/600000	130	1.7 x 10^{-17}

[a) MW = molecular weight

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