

Nanoscale Mixing of Soft Solids

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ABSTRACT: Assessing the state of mixing on the molecular scale in soft solids is challenging. Concentrated solutions of micelles formed by self-assembly of polystyrene-*block*-poly(ethylene-*alt*-propylene) (PS-PEP) diblock copolymers in squalane (C₃₀H₆₂) adopt a body-centered cubic (bcc) lattice, with glassy PS cores. Utilizing small-angle neutron scattering (SANS) and isotopic labeling (¹H and ²H (D) polystyrene blocks) in a contrast-matching solvent (a mixture of squalane and perdeuterated squalane), we demonstrate quantitatively the remarkable fact that a commercial mixer can create completely random mixtures of micelles with either normal, PS(H), or deuterium-labeled, PS(D), cores on a well-defined bcc lattice. The resulting SANS intensity is quantitatively modeled by the form factor of a single spherical core. These results demonstrate both the possibility of achieving complete nanoscale mixing in a soft solid and the use of SANS to quantify the randomness.

Mixing and unmixing of ingredients, from simple elements like iron and carbon (e.g., steel) to complex gastronomical preparations (e.g., mayonnaise), represent some of the most important and demanding facets of modern chemical technology. Combining thermodynamically compatible liquids such as water and methanol is trivial, whereas blending inorganic solids (glassy or crystalline materials) is virtually impossible. Soft materials present complications in processing that reflect both limits of behavior. Although susceptible to deformation and flow, biological tissues, colloids, liquid crystals, pharmaceutical active agents and excipients, and polymer melts all display complex and often delicate thermodynamic and dynamic properties that frequently challenge mixing strategies. For example, polymer melts are both viscous and elastic with relaxation times that are highly dependent on molecular weight. Moreover, asymptotically small entropies of mixing render most polymers incompatible,¹ even polyolefin isomers such as polyethylene and polypropylene. Determining the state of mixing in soft materials at the molecular scale can be extraordinarily challenging, yet the detailed arrangement of components often determines the performance of a product. This Communication describes a simple process for blending soft solids comprising ordered block copolymer micelles and, most significantly, demonstrates uniform nanoscale mixing using a small-angle neutron scattering (SANS) technique.

Recently we reported on the structure² and molecular exchange dynamics³ of micelle-forming poly(styrene-*block*-ethylene-*alt*-propylene) (PS-PEP) diblock copolymers dispersed in

squalane (C₃₀H₆₂), a low-volatility saturated hydrocarbon solvent. These micelles, which contain a solvophobic PS core (glass transition $T_{g,PS} \cong 70$ °C) and a corona of solvated PEP blocks, are distributed isotropically at low concentrations (<7% block copolymer) but order on a body-centered cubic (bcc) lattice at higher concentrations.² The rate of block copolymer exchange between the disordered micelles was characterized at elevated temperatures ($100 \leq T \leq 145$ °C) by monitoring the change in SANS intensity following blending of normal (PS(H)-PEP) and deuterium-labeled (PS(D)-PEP) micelles (1 vol%) at room temperature.³ We employed an isotopically labeled squalane mixture (C₃₀H₆₂ and C₃₀D₆₂) such that complete mixing of the PS(D) and PS(H) blocks produced a core scattering length density that exactly matched the average solvent value, thereby extinguishing coherent elastic scattering from the spherical domains. Because these solutions are liquids, simple stirring ensures rapid and complete micelle mixing at room temperature (where the PS cores are glassy), prior to probing molecular exchange at elevated temperatures. However, establishing the extent of mixing at nanoparticle length scales for soft yet solid-like materials, such as ordered PS-PEP micelles in squalane, is considerably more challenging. Here we demonstrate that perfectly random nanoscale mixing of macroscopically ordered (bcc) block copolymer solutions can be achieved using a commercial laboratory-scale mixer, as documented by SANS based on a contrast-matching technique (see Figure 1).

Nearly equivalent PS(H)- and PS(D)-PEP diblock copolymers were synthesized by anionic polymerization of styrene and isoprene followed by catalytic saturation of the polyisoprene blocks with deuterium as described elsewhere.² The molecular characteristics, determined by size exclusion chromatography and ¹H NMR spectroscopy, are as follows: $M_n(\text{PS(H)-PEP}) = 26\text{--}68$ kg/mol and $M_w/M_n = 1.04$; $M_n(\text{PS(D)-PEP}) = 27\text{--}70$ kg/mol and $M_w/M_n = 1.10$. Polymer solutions containing 15 vol% block copolymer were prepared by dissolving either PS(H)- or PS(D)-PEP in dichloromethane along with a partially deuterium-labeled squalane mixture (42 vol% C₃₀H₆₂ and 58 vol% C₃₀D₆₂), followed by evaporation of the dichloromethane at room temperature and annealing at 150 °C for 5 min.

SANS experiments were performed with the NG7 30m instrument at the Center for Neutron Research located at the National Institute of Standards and Technology, Gaithersburg, MD, using $\lambda = 7$ Å neutrons ($\Delta\lambda/\lambda = 0.11$) and a sample-to-detector-distance of 11 m. Small-angle X-ray scattering (SAXS) measurements were conducted with the instrument maintained by the DuPont-Northwestern-Dow Collaborative Access Team at

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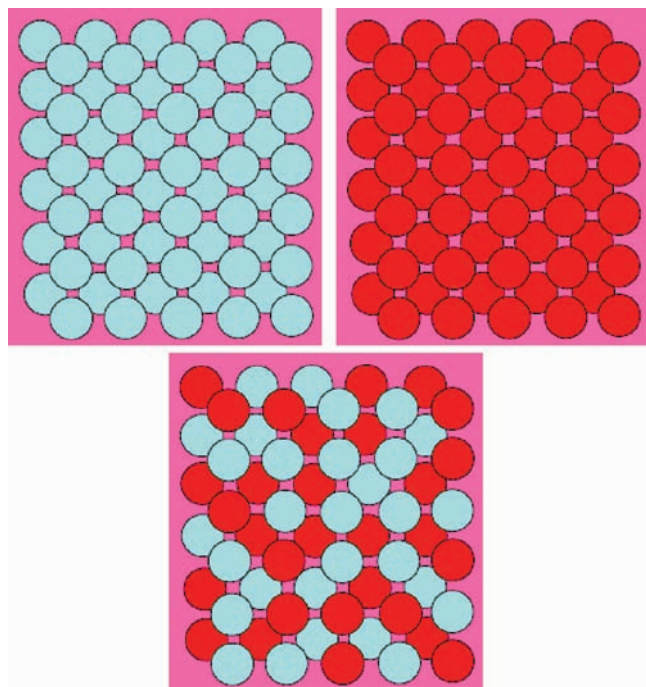


Figure 1. Illustration of PS(D) (blue) and PS(H) (red) spheres ordered on a crystalline lattice and immersed in a contrast-matched matrix of squalane ($C_{30}H_{62} + C_{30}D_{62}$) (purple). SANS from either upper panel results in Bragg diffraction (Figure 2), while random placement of the red and blue spheres (lower panel) extinguishes interparticle interference, thus exposing single-sphere scattering as shown in Figure 5.

Argonne National Laboratory. Radiation of 17 keV, corresponding to a wavelength $\lambda = 0.729 \text{ \AA}$, and a sample-to-detector distance of 6.6 m were employed.

Figure 2 shows SANS powder patterns (intensity I versus scattering wave vector magnitude $|q| = q = 4\pi\lambda^{-1} \sin(\theta/2)$, where θ is the scattering angle) recorded from the 15 vol% PS(D)- and PS(H)-PEP mixtures in the isotopic squalane solvent. Three Bragg peaks are evident in each data set, which derive from the packing of spherical micelles on a bcc lattice with unit cell parameters $a_{\text{bcc}} = 68$ (PS(D)-PEP) and 62 nm (PS(H)-PEP). SAXS results (inset to Figure 2) confirm this structural assignment. We attribute the small difference in lattice parameters evidenced by the slight difference in Bragg peak positions to the minor variation in molecular weights and polydispersities of the block copolymer specimens.

Dynamic mechanical spectroscopy measurements, obtained at 30 °C from a 15 vol% PS(H)-PEP solution (normal squalane) using an ARES rheometer (fitted with 25 mm parallel plates), are presented in Figure 3. The results in Figure 3a are typical of well-ordered, triply periodic soft solids: the linear dynamic elastic modulus $G' \approx 400 \text{ Pa}$ (0.5% strain amplitude) dominates the viscoelastic response (dynamic loss modulus $G'' \ll G'$) in the limit $\omega \rightarrow 0$, where ω is the measurement frequency.^{4–6} Increasing the magnitude of the sinusoidal strain amplitude leads to a breakdown of the ordered (bcc) structure, as illustrated in Figure 3b for $\omega = 1 \text{ rad/s}$. A precipitous drop in G' and a corresponding rise in G'' at strain amplitudes above about 10% indicate disruption of the soft solid, due to either the generation of dislocations accompanied by plastic flow or perhaps shear-induced melting.⁷ This process is reversible, and cessation of shear leads to complete recovery of the linear response G' and G'' values shown in Figure 3a.

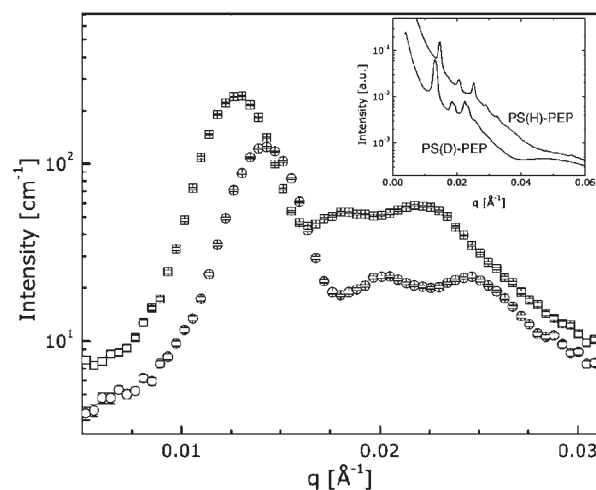


Figure 2. SANS patterns obtained from 15 vol% PS(D)-PEP (squares) and PS(H)-PEP (circles) in an isotopic squalane mixture (42 vol% $C_{30}H_{62}$ and 58 vol% $C_{30}D_{62}$) at 30 °C. Inset shows the corresponding synchrotron SAXS patterns.

Complete mixing of batches of soft solids requires the application of flow fields capable of driving the components together down to nanometer length scales. Direct verification of homogenization is generally difficult or impossible. However, SANS from the model system considered here, comprising equal amounts of PS(H)- and PS(D)-PEP micelles distributed in squalane, can be treated exactly, providing a quantitative method for evaluating the efficiency of mixing. For a blend containing equal numbers ($N_{\text{H}} = N_{\text{D}} = N/2$) of perfectly randomly mixed and identically sized normal and deuterated spheres, the neutron scattering intensity can be represented by the sum of intraparticle, $P(q)$, and interparticle, $Q(q)$, correlations,⁸

$$\frac{I(q)}{A} = \left[\frac{(\Delta\rho_{\text{H}})^2 + (\Delta\rho_{\text{D}})^2}{2} \right] P(q) + \left[\frac{\Delta\rho_{\text{H}} + \Delta\rho_{\text{D}}}{2} \right]^2 NQ(q) \quad (1)$$

where the constant $A = \nu^2 z^2 N/V$ is determined by the z scattering centers of volume ν per sphere and the overall system volume V . The intensity of scattered neutrons is controlled by the differences in scattering length densities, $\Delta\rho_{\text{H}} = \rho_{\text{H}} - \rho_{\text{S}}$ and $\Delta\rho_{\text{D}} = \rho_{\text{D}} - \rho_{\text{S}}$ (ρ_{S} refers to the isotopic squalane solution), in which $\rho_i = (b/\nu)_i$, where $b = \sum b_i$ is the sum of atomic coherent scattering lengths per volume element ν . For solid spherical particles the form factor is given by

$$P(q) = 9 \left[\frac{\sin(qR) - (qR) \cos(qR)}{(qR)^3} \right]^2 \quad (2)$$

where R is the hard-sphere radius, i.e., the PS core radius in the present case. A more complete examination of eq 1 will be presented in a separate publication.⁹ The scattering length densities are collected in Table 1.

Interparticle (sphere–sphere) interference is accounted for in eq 1 by $Q(q)$. For ordered systems this parameter is governed by the phase factors associated with a given crystal symmetry and the associated planar (hkl) spacings leading to Bragg peaks at specific ratios of q values; for bcc packing, $(q/q^*)^2 = 1, 2, 3, 4, 5, 6, 7, \dots$, where q^* is the position of the first reflection.¹⁰ Disordered ensembles of spheres produce one or two broad interparticle

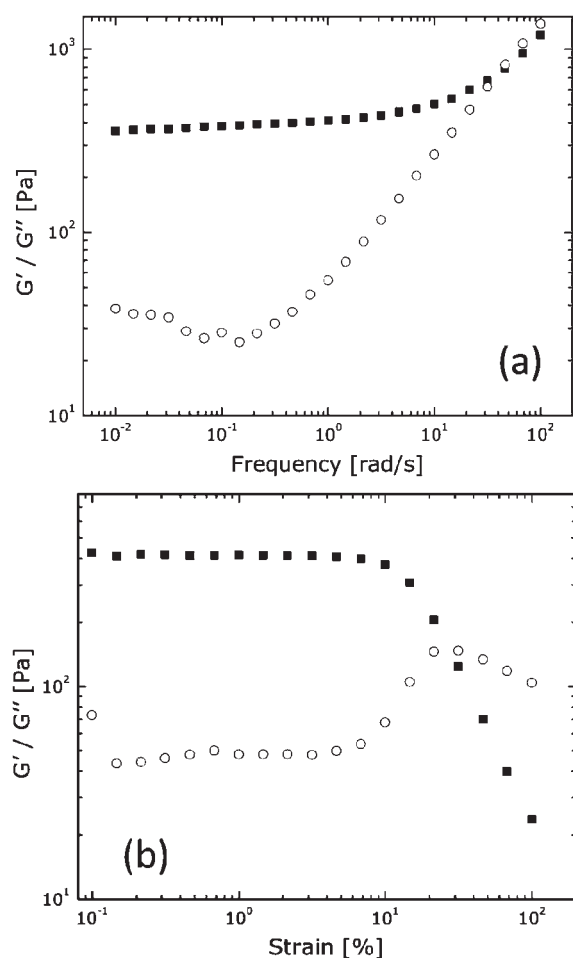


Figure 3. (a) Frequency dependence of G' and G'' (0.5% strain amplitude) for 15 wt% PS(H)-PEP in squalane at 30 °C. (b) Strain amplitude dependence of G' and G'' determined with a frequency $\omega = 1$ rad/s. These dynamic mechanical spectroscopy experiments demonstrate that the diblock copolymer solution is a soft solid (bcc by SAXS) characterized by a linear elastic shear modulus below about 10% strain amplitude.

Table 1. Mass and Scattering Length Densities

material	formula	density (g/cm ³) ^a	ρ (10 ¹⁰ cm ⁻²)
dPS	C ₈ D ₈	1.128	6.46
hPS	C ₈ H ₈	1.047	1.41
PEP	C ₃ D _{2.3} H _{7.7}	0.884	1.46
d-squalane	C ₃₀ D ₆₂	0.929	7.08
h-squalane	C ₃₀ H ₆₂	0.810	-0.374

^a Density of deuterated material calculated assuming the same volume as the protonated equivalent.

scattering peaks that can be interpreted on the basis of an isotropic (liquid-like) radial distribution function. Inspection of eq 1 reveals that the contribution from interparticle scattering can be eliminated by setting $\rho_S = (\rho_H + \rho_D)/2$, provided that the isotopically labeled spherical particles are randomly distributed throughout the material. The squalane composition (42 vol% C₃₀H₆₂ and 58 vol% C₃₀D₆₂) used with the PS(H)- and PS(D)-PEP diblock copolymers exactly satisfies this criterion. (Here we note that we have ignored scattering from the solvated PEP

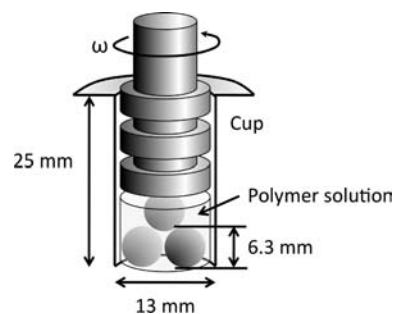


Figure 4. Schematic illustration of the MiniMAX mixer (CSI Co.) employed to blend ordered block copolymer mixtures. The specimen is held in a cup, along with three balls that facilitate mixing, confined by a rotor that applies a macroscopic shear stress. Separate 15% solutions of PS(D)- and PS(H)-PEP in the isotopic squalane mixture were combined at room temperature using a steady rotation rate of 115 rpm, corresponding to an estimated shear rate $\dot{\gamma} \approx 10$ s⁻¹.

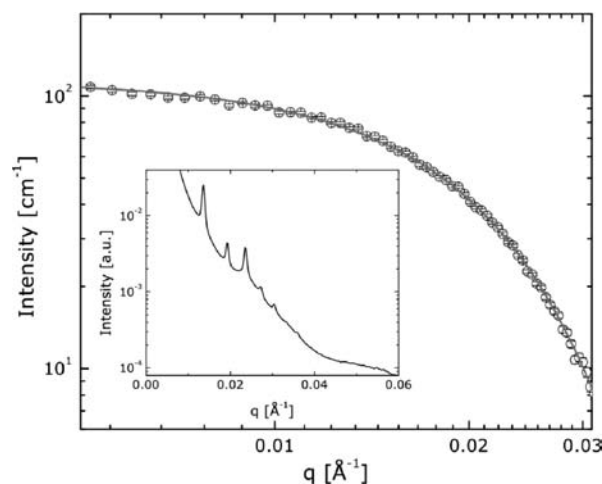


Figure 5. SANS pattern obtained from the mechanically blended PS(H)- and PS(D)-PEP solutions (each 15 vol% in contrast-matched squalane) at 30 °C. The solid curve represents a best fit to the spherical form factor. A synchrotron SAXS pattern (inset) obtained from the same mixture confirms a bcc crystal structure.

blocks and from fluctuations in sphere size, both of which have been shown to be insignificant (<2%) relative to the contributions from the single-particle core scattering.^{3,9}

We employed a MiniMax mixer (CSI Co.)^{11,12} to combine equal volumes of the 15% PS(H)- and PS(D)-PEP squalane mixtures at room temperature. This device (shown schematically in Figure 4) requires approximately 0.5 g of material and subjects the components to a combination of extensional and shearing flows, aided by the presence of three small mixing balls. Because the PS cores are glassy at room temperature, the constituent block copolymers are not able to exchange between micelles, thus ensuring the integrity of the isotopically labeled cores; this assumption is confirmed by measurements of chain exchange kinetics at much higher temperatures.^{3,9}

Figure 5 shows SANS data obtained from a specimen that was mixed for 25 min at a rotation rate of 115 rpm, corresponding to the estimated shear rate $\dot{\gamma} \approx 10$ s⁻¹; the actual shear rate may be higher due to the presence of the balls. Clearly, all evidence of Bragg scattering has been suppressed, and the resulting scattering pattern is quantitatively accounted for by the hard-sphere form

factor given by eq 2 (solid curve) with $R = 11.0$ nm. An independent synchrotron SAXS measurement (inset of Figure 5) verifies that this blended sample retains a well-defined bcc crystal structure; on the basis of the specimen composition and the bcc lattice parameter determined by SAXS, we calculate $R = 10.7$ nm, which within experimental error equals the SANS-based value. This result demonstrates remarkably efficient and complete mixing of two soft solids at all length scales down to the fundamental system dimension, the micelle core radius.

Contrast-matching represents a unique and powerful capability of neutron scattering, one that has been exploited since the first compilation of isotope-dependent neutron scattering lengths by Shull and Wollan in 1951.^{13,14} Five years later, Sidhu et al.¹⁵ elegantly showed that all coherent neutron diffraction from a solid-state (hexagonal close-packed) solution of titanium ($b_{\text{Ti}} = -0.38 \times 10^{-12}$ cm) and zirconium ($b_{\text{Zr}} = 0.62 \times 10^{-12}$ cm) is extinguished in crystalline powders containing 62 atom% titanium. This is exactly analogous to the result obtained with the randomly blended PS(H)- and PS(D)-PEP micelles, where every plane of randomly arranged normal and deuterated spheres in the bcc crystal contains an average scattering length density that matches the squalane matrix. For atomic crystals (e.g., Ti and Zr), a minuscule nuclear diameter ($\sim 10^{-5}$ nm) makes intraparticle scattering irrelevant ($P(q) \rightarrow 1$ in this limit) and leads to a matrix with essentially zero neutron scattering length density (i.e., filled only with electrons). For the situation involving spherical particles with diameters comparable in size to the crystal lattice dimensions, as illustrated in Figure 1, both intra- and interparticle scattering must be accounted for, including a finite matrix term ρ_{S} , as summarized by eq 1 for the case where $N_{\text{H}} = N_{\text{D}}$.

The first applications of SANS to isotopic polymer mixtures in 1972^{16,17} ushered in a host of new experimentation that continues to expand our knowledge of macromolecular and soft matter structure today. Contrast-matching of block copolymers has been exploited over the past two decades, for example to eliminate Bragg diffraction in order to expose single-chain scattering from polymer chains within microphase-separated domains.^{18–23} While these past examples of contrast-matching are governed by the same general principles that lead to eq 1, we are not aware of any previous study that has exploited the added constraint of random particle placement in an ordered system for the purpose of characterizing soft solids.

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