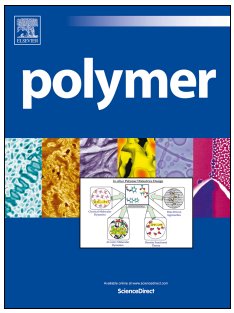

Quantitative examination of a fundamental assumption in small-angle neutron scattering studies of deformed polymer melts

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PII: S0032-3861(20)30528-0

DOI: https://doi.org/10.1016/j.polymer.2020.122698

Reference: JPOL 122698

To appear in: *Polymer*

Received Date: 18 March 2020

Revised Date: 1 June 2020

Accepted Date: 4 June 2020

Please cite this article as: Wang Y, Wang W, Hong K, Do C, Chen W-R, Quantitative examination of a fundamental assumption in small-angle neutron scattering studies of deformed polymer melts, *Polymer* (2020), doi: https://doi.org/10.1016/j.polymer.2020.122698.

Yangyang Wang: Conceptualization, Methodology, Resources, Investigation, Formal analysis, Writing – Original Draft, Writing-Review & Editing, Funding acquisition

Weiyu Wang: Resources

Kunlun Hong: Resources

Changwoo Do: Resources, Investigation

Wei-Ren Chen: Resources, Investigation

Quantitative examination of a fundamental assumption in small-angle neutron scattering studies of deformed polymer melts

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Abstract

It has long been established that the coherent scattering intensity of neutrons by isotropic mixtures of hydrogenous and deuterated polymers of matching molecular weights is, to the first approximation, proportional to the single-chain structure factor of the polymer chain. The validity of this fundamental relation for equilibrium, undeformed polymer melts is well supported by the extensive experimental and theoretical investigations over the past several decades. The generalization of this relation to the case of nonequilibrium, deformed polymer melts, however, is not a trivial one. Despite its widespread usage in small-angle neutron scattering (SANS) studies of deformed polymer melts, the assumed proportionality between coherent scattering intensity and single-chain structure factor has received very little experimental scrutiny. This work quantitatively examines this issue through spherical harmonic expansion analysis of the anisotropic SANS spectra of deformed polystyrene melts of different levels of deuterium labeling. It is shown that the classical assumption works extremely well over a wide range of scattering wavevectors, where the isotropic component of the SANS spectrum and the leading term of structural anisotropy vary by more than two orders of magnitudes.

Keywords: Small-angle neutron scattering, polymer melts, rheology

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1. Introduction

Small-angle neutron scattering (SANS) is a powerful experimental technique for examining the conformational changes of polymers under flow and deformation and has been widely applied in rheological studies of polymer solutions [1-3] and melts [4-19]. For isotopically labeled polymer melts consisting of hydrogenous and deuterated chains of comparable lengths, extensive experimental and theoretical studies have shown that the coherent scattering intensity from such systems in the quiescent state is proportional to the single-chain structure factor (form factor) of the polymer. This important result has been generalized to the case of nonequilibrium state – polymers under flow and deformation. Indeed, it has been the working hypothesis in the past 40 years or so that the coherent scattering intensity $I_{\mathrm{coh}}(\boldsymbol{Q})$ from *deformed*, isotopically labeled polymer melts directly reflects the *anisotropic* single-chain structure factor $S_{\mathrm{chain}}(\boldsymbol{Q})$:

$$I_{\mathrm{coh}}(\boldsymbol{Q}) \propto S_{\mathrm{chain}}(\boldsymbol{Q}). \tag{1}$$

Despite the central role of this assumption in SANS studies of polymer rheology, there has been only one experimental study that explicitly examines its validity [20]. Additionally, this early pioneering work suffers a few drawbacks,[1] and has not completely resolved the issue. Taking advantage of the spherical harmonic expansion (SHE) technique [4, 5, 21-28], this study re-examines the aforementioned fundamental assumption in small-angle neutron scattering investigations of deformed polymers in a quantitative and rigorous manner. From a scientific viewpoint, the contributions of this work are threefold. First, the SHE method allows one to extract and quantify the isotropic and anisotropic components of the 2D SANS spectra over a

[1] First, the chain lengths of the protonated and deuterated polystyrenes were not perfectly matched in the work of Boué *et al.*[20], with the degree of polymerization of the protonated chain 17% higher than that of the deuterated chain. Second, no rheological data were described in this work. It's unclear whether the sampled examined by SANS exhibited identical stress-strain behavior under tension. Third, for the stretched samples, the SANS data were only reported over a rather limited Q range. And the two-dimensional SANS spectrum was not fully utilized – only the scattering intensities in the parallel and perpendicular directions were analyzed. Lastly, the low-Q behavior cannot be clearly resolved by the inverse intensity plot ($1/I(Q)$ vs. Q^2).

wide range of scattering wavevectors. This provides a robust route to rigorously examining the fundamental assumption in small-angle neutron scattering studies of deformed polymer melts (Eq. 1). Second, we explicitly show that the samples for the scattering investigation indeed exhibit identical rheological behavior, in both the linear and nonlinear viscoelastic regimes. Lastly, our experiments are based on carefully designed model systems: the degrees of polymerization of the deuterated and hydrogenous components differ by only a few percent, with their polydispersity index (PDI) extremely close to unity. These improvements allow us to draw a definitive conclusion on the validity of Eq. (1), removing any lingering doubt about this long-held assumption.

Besides the apparent scientific motivation, this investigation also serves a pedagogical purpose. While the application of small-angle neutron scattering to polymer rheology has a long history, some practitioners are not familiar with the theoretical framework for formulating and interpreting experiments. In particular, many systems of practical interest, from the point of view of scattering, are far more complicated than the classical case of isotopically labeled melts. By dissecting the small-angle neutron scattering theory and experiment involving a simple system of hydrogenous and deuterated chains of identical degree of polymerization, we expose the underlying fabric for data interpretation. This exercise may serve as a useful reference for future studies of complex systems, where analysis and interpretation of anisotropic SANS spectra can be much more challenging.

2. Theoretical background

2.1. Traditional theoretical argument

Before delving into the experimental details, we pause to review the traditional theoretical argument that leads to Eq. (1) for *deformed* polymers. As a special case, the validity of Eq. (1)

has been extensively tested in undeformed, isotropic polymer melts [20, 29, 30], where the scattering intensity has no dependence on the polar angle. Specifically, the coherent scattering intensity from isotopically labeled polymer melts consisting of hydrogenous and deuterated chains of identical lengths is given by

$$I_{\mathrm{coh}}(\boldsymbol{Q}) = (b_{\mathrm{D}} - b_{\mathrm{H}})^2 \varphi(1-\varphi) n_{\mathrm{seg}} N S(\boldsymbol{Q}), \tag{2}$$

where b_{D} and b_{H} are the coherent scattering length of the deuterated and hydrogenous chain segments ("repeating units"), respectively, φ is the volume fraction of the hydrogenous chains, n_{seg} is the polymer segment number density, and N is the degree of polymerization of the polymer chain (*i.e.*, number of segments per chain). $S(\boldsymbol{Q})$ is the single-chain structure factor of the polymer chain: $S(\boldsymbol{Q}) \equiv S_{\mathrm{chain}}(\boldsymbol{Q})$. From this point onwards, we will drop the subscript "chain" and use $S(\boldsymbol{Q})$ to denote the single-chain structure factor in this article, unless otherwise stated. Since the scattering intensity from an isotropic sample does not depend on the orientation of $\boldsymbol{Q}$, Eq. (2) is often written as $I_{\mathrm{coh}}(Q) = (b_{\mathrm{D}} - b_{\mathrm{H}})^2 \varphi(1-\varphi) n_{\mathrm{seg}} N S(Q)$, where Q is a scalar. As a classical formula, Eq. (2) has been derived and re-derived numerous times in the literature by different authors through various methods [31-35]. Here we review the argument presented by Higgins and Benoît in their book on polymers and neutron scattering [32] and point out that *no explicit assumption* about the sample anisotropy has been made in this derivation. In other words, their argument can be applied to both isotropic and deformed polymers. However, we must realize that this fact alone does not guarantee the validity of Eq. (2) for the deformed state. As a cautionary tale, we will demonstrate at the end of this article that a similar but more general formula for polymer blends is valid for the isotropic state but fails when the polymers are deformed. In this case, there is no *explicit* assumption about the sample anisotropy in the

theoretical argument, either. Because of the subtlety of the issue, a direct and careful experimental examination of Eq. (2) appears rather necessary.

For a mixture of hydrogenous (ordinary) and deuterated chains, the coherent scattering intensity for a given volume can be expressed as

$$I_{\mathrm{coh}}(\boldsymbol{Q}) = b_{\mathrm{H}}^2 S_{\mathrm{HH}}(\boldsymbol{Q}) + 2b_{\mathrm{H}}b_{\mathrm{D}}S_{\mathrm{HD}}(\boldsymbol{Q}) + b_{\mathrm{D}}^2 S_{\mathrm{DD}}(\boldsymbol{Q}), \tag{3}$$

where $S_{\alpha\beta}$ is the partial structure factor defined as $S_{\alpha\beta}(\boldsymbol{Q}) = \sum_{i=1}^{N_\alpha}\sum_{j=1}^{N_\beta}\langle e^{-\mathbb{i}\boldsymbol{Q}\cdot(\boldsymbol{r}_i-\boldsymbol{r}_j)}\rangle$, with N_α and N_β being the total number of chain segments for species α and β, respectively. Under the assumption of incompressibility, which is typically true for polymeric liquids on large length scales, we have $\Delta n_{\mathrm{H}}(\boldsymbol{r}) + \Delta n_{\mathrm{D}}(\boldsymbol{r}) = 0$, where Δn_{H} and Δn_{D} are the fluctuations of number density for the hydrogenous and deuterated chain segments, respectively. Here, the *implicit* assumption is that the molecular volumes of the hydrogenous and deuterated segments are the same. With this incompressibility condition, it can be shown that

$$S_{\mathrm{HH}}(\boldsymbol{Q}) = S_{\mathrm{DD}}(\boldsymbol{Q}) = -S_{\mathrm{HD}}(\boldsymbol{Q}). \tag{4}$$

The details of this fundamental result for small-angle neutron scattering are further discussed in Appendix A. Using Eq. (4), we can rewrite Eq. (3) as

$$I_{\mathrm{coh}}(\boldsymbol{Q}) = (b_{\mathrm{H}} - b_{\mathrm{D}})^2 S_{\mathrm{HH}}(\boldsymbol{Q}) = (b_{\mathrm{H}} - b_{\mathrm{D}})^2 S_{\mathrm{DD}}(\boldsymbol{Q}) = -(b_{\mathrm{H}} - b_{\mathrm{D}})^2 S_{\mathrm{HD}}(\boldsymbol{Q}). \tag{5}$$

As is well known, a more general form of Eq. (5) can be conveniently expressed in terms of scattering length density, when the molecular volumes of the hydrogenous and deuterated chain segments are different. Evidently, this subtle point has no essential bearing on the current problem, as it only involves the proportionality constant between $I_{\mathrm{coh}}(\boldsymbol{Q})$ and $S_{\alpha\beta}(\boldsymbol{Q})$.

As shown in Appendix A, Eq. (5) is supposed to be valid for both isotropic and deformed states. Furthermore, in the case of mixtures of hydrogenous and deuterated chains of identical degree of polymerization, Eq. (5) directly leads to the prediction that $I_{\mathrm{coh}}(\boldsymbol{Q}) \propto S_{\mathrm{chain}}(\boldsymbol{Q})$, when

the mixing of the two polymers is ideal (see Appendix B), without any requirement about structural symmetry. In other words, the classical theory asserts that for incompressible, ideally mixed hydrogenous and deuterated polymers of identical chain lengths, the coherent scattering intensity is always proportional to the single-chain structure factor, regardless of the deformation state. As pointed out in the Introduction, despite the extensive experimental evidence supporting Eq. (1) in the isotropic, equilibrium state, the anisotropic, nonequilibrium case has not been adequately studied. From a theoretical perspective, an obvious lingering question is whether non-ideal mixing of hydrogenous and deuterated chains would pose a serious problem for data interpretation in the deformed state.

2.2. Spherical harmonic expansion analysis

Boué's previous neutron scattering study on this subject [20] examines the intensities from uniaxially stretched polymers in the parallel and perpendicular directions. This approach, however, does not fully exploit the two-dimensional SANS spectra of the deformed polymers [5]. The current investigation takes advantage of the spherical harmonic expansion framework [4, 5, 21-28], which permits quantitative analysis of small-angle scattering spectra. For the current problem of small-angle neutron scattering by deformed polymers, the intensity at low Q is completely dominated by coherent scattering. We define a structure factor $S(\boldsymbol{Q})$ of the polymer melt: $S(\boldsymbol{Q}) \equiv I(\boldsymbol{Q})/\lim_{Q\to 0} I_{\mathrm{iso}}(Q)$. $S(\boldsymbol{Q})$ takes on the meaning of the single-chain structure factor when Eq. (2) applies. More generally, $S(\boldsymbol{Q})$ can be simply regarded as a normalized scattering intensity, as the validity of Eq. (2) is the very subject of this investigation. For uniaxial extension, $S(\boldsymbol{Q})$ can be expanded by spherical harmonics as

$$S(\boldsymbol{Q}) = \sum_{l:\mathrm{even}} S_l^0(Q) Y_l^0(\theta, \phi), \tag{6}$$

where $Y_l^0(\theta,\phi)$ is the real spherical harmonic function of degree l and order zero and $S_l^0(Q)$ is the corresponding Q-dependent expansion coefficient. Figure 1 illustrates the details of the scattering geometry, where the stretching direction coincides with the z axis and the detector plane is parallel to the xz plane. As explained in Ref. [5], the relevant spherical harmonics for uniaxial extension are essentially all the even degree Legendre functions: $Y_l^0(\theta,\phi) = \Theta_l(\theta) = \sqrt{2l+1}P_l(\cos\theta)$, and the expansion coefficients $S_l^0(Q)$ can be straightforwardly obtained from the 2D SANS spectra as $S_l^0(Q) = \frac{1}{2}\int_0^\pi \sin\theta\, d\theta\, I_{xz}(Q,\theta)\Theta_l(\theta)/\lim_{Q\to 0} I_{\text{iso}}(Q)$.

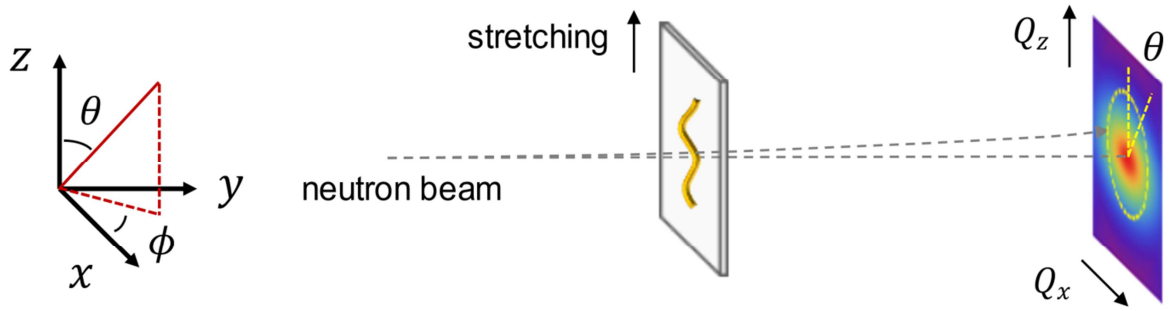

Fig. 1. Illustration of the scattering geometry. The stretching direction is along the z axis and the two largest flat surfaces (xz plane) of the rectangular sample are perpendicular to the incident neutron beam. θ is the polar angle from the positive z axis with $\theta \in [0,\pi]$ and ϕ is the azimuthal angle in the xy plane from the x axis with $\phi \in [0,2\pi)$.

2.3. Design philosophy of the experiment

To examine the assumption that the anisotropic coherent scattering intensity from isotopically labeled, deformed polymer melts is proportional to the single-chain structure factor, *i.e.*, $I_{\text{coh}}(\boldsymbol{Q}) \propto S_{\text{chain}}(\boldsymbol{Q})$, we perform small-angle neutron scattering experiments on samples with various h/d ratios, uniaxially stretched under identical conditions. In our current context, the measured scattering intensity $I(\boldsymbol{Q})$, according to the traditional theoretical argument, can be expressed in the following form:

$$I(\boldsymbol{Q},\varphi) = I_0(\varphi)S_{\text{chain}}(\boldsymbol{Q}) + I_{\text{bkg}}(\varphi), \quad (7)$$

where the $I(\boldsymbol{Q},\varphi)$, zero-angle coherent scattering intensity $I_0(\varphi)$, and "background" $I_{\text{bkg}}(\varphi)$ depend on the volume fraction of the hydrogenous polymer, but the single-chain structure factor $S_{\text{chain}}(\boldsymbol{Q})$ does not. Therefore, our goal is to test whether the apparent anisotropic single-chain structure factor, defined as $S(\boldsymbol{Q}) \equiv [I(\boldsymbol{Q}) - I_{\text{bkg}}]/I_0$, is indeed independent of the sample composition. The previous investigation by Boué and coworkers [20] examined the structures of $S(\boldsymbol{Q})$ only in parallel and perpendicular directions to stretching, without a complete analysis of the 2D SANS spectra. Additionally, their inverse intensity plot ($1/I(Q)$ vs. Q^2) placed emphasis on the high-Q region, making it difficult to resolve the behavior at low Qs. In contrast, by employing the spherical harmonic expansion technique outlined in the preceding section, this study quantitatively surveys the full anisotropic structures in a broad range of scattering wavevectors. Specifically, we will compare the expansion coefficients $S_l^0(Q)$ of different samples to see if the degree of isotope labeling has any impact on the result.

3. Materials and methods

3.1.Sample preparation

Our experimental system is a blend of deuterated (*d*-PS) and hydrogenous polystyrenes (*h*-PS) of matching degree of polymerization. The deuterated polystyrene (with M_w=253 kg/mol and M_n=252 kg/mol) was synthesized by anionic polymerization in benzene with *sec*-butyllithium as the initiator. The hydrogenous polystyrene (with M_w=222 kg/mol and M_n=218 kg/mol) was purchased from Polymer Source. The *h*-PS and *d*-PS are dissolved in toluene at five different *h*/*d* ratios (2:98, 4:96, 8:92, 16:84, and 32:68) and precipitated in excess methanol. The resulting blends were dried in a vacuum oven first at room temperature for approximately six hours and then at 130°C for more than 12 hours (overnight) to completely remove the residual solvent. The

linear viscoelastic properties of these polymer mixtures were characterized by small-amplitude oscillatory shear measurements in the temperature range from 120 to 200°C on a DHR2 rheometer (TA Instruments) with parallel-plate geometry (8mm in diameter). The temperature was controlled by DHR2's convection Environment Test Chamber with nitrogen as the gas source.

To prepare for the small-angle neutron scattering experiments, the isotopically labeled polystyrenes were molded into rectangular specimens on a Carver hydraulic press at 200°C. They were then uniaxially stretched on an RSA-G2 Solid Analyzer with a constant engineering strain rate of $0.02\ s^{-1}$ (*i.e.*, constant crosshead velocity) to a stretching ratio of $\lambda = 1.8$ at 125°C. Immediately after the deformation, cold nitrogen gas were introduced to the convection oven of the RSA-G2 to quenched the stretched sample into a glassy state. According to the estimates presented in Section 4, the longest chain relaxation time τ and the Rouse relaxation time τ_R of the polystyrene[2] are 6.87×10^3 and 279 s, respectively, at 125°C. As a result, the instantaneous Rouse Weissenberg number $\dot{\epsilon}\tau_R$ was greater than unity throughout the stretching experiment. Additionally, the long relaxation times ensured that molecular relaxation was negligible during the quenching procedure.

3.2.Small-angle neutron scattering

Small-angle neutron scattering measurements of both the isotropic and deformed polystyrene samples were performed on the EQ-SANS beamline of the Spallation Neutron Source (Oak Ridge, TN). The scattering geometry is shown in Fig. 1, where the stretching direction is along the z axis and the flat surfaces (xz plane) of the rectangular sample are perpendicular to the

[2] Since the chain lengths of the *h*-PS and *d*-PS are closely matched, we do not make a distinction between the two polymers here and ignore the subtle changes of relaxation times with the *h*/*d* ratio. This simplification avoids redundancy in the discussion.

incident neutron beam. The polymer sample was held in place by two quartz windows in a standard demountable titanium sample cell. A total of three instrument configurations were used to cover a Q range from approximately 0.004 to 0.2 Å^{-1}. The measured intensity was corrected for sample transmission, sample cell scattering, detector background and sensitivity, and placed on the absolute scale by using measurement of a standard sample.

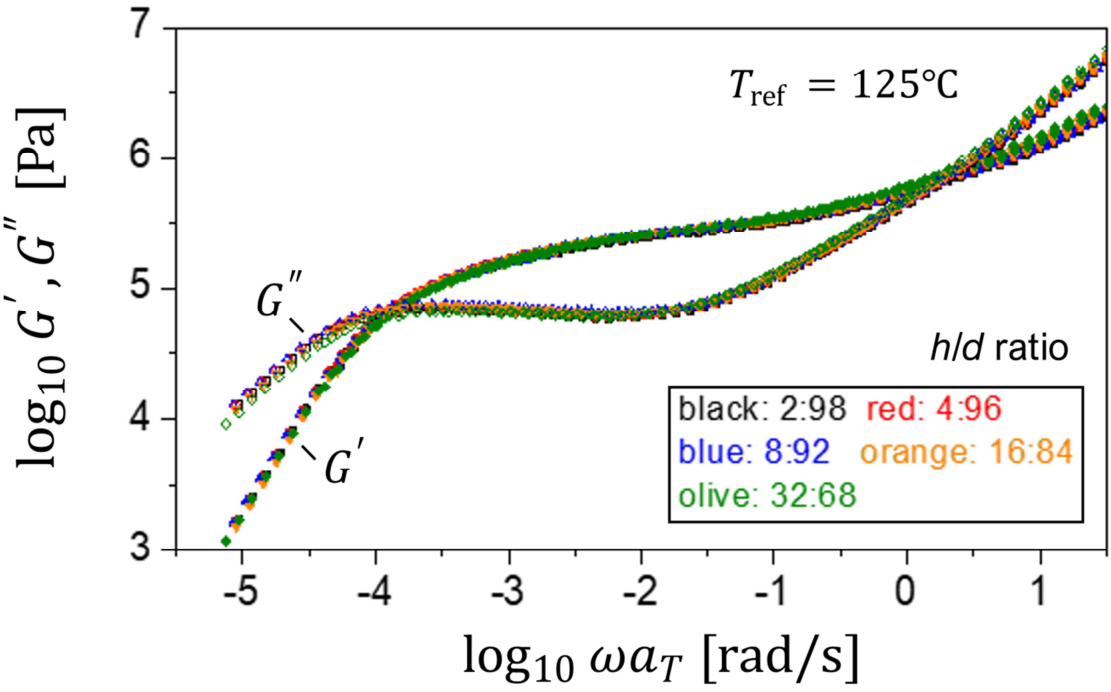

Fig. 2. Linear viscoelastic spectra of the polystyrene samples of different *h*/*d* ratios, constructed by using the Time-Temperature Superposition (TTS) Principle. a_T is the shift factor for the TTS procedure. The reference temperature is 125°C. Solid symbols: $G'(\omega)$. Open symbols: $G''(\omega)$.

4. Results and discussion

4.1.Equilibrium properties

To improve upon the previous effort [20] to establish the validity of Eq. (1) in the *nonequilibrium* state, we first try to match the length of the hydrogenous and deuterated chains as closely as possible. Since the rheology of entangled polymers is sensitive to molecular weight,

mismatch in chain length can result in different rheological responses as we vary the *h*/*d* ratio of the samples. Fig. 2 shows the dynamic moduli [$G'(\omega)$ and $G''(\omega)$] of the polystyrene samples of different *h*/*d* ratios, constructed by using the Time-Temperature Superposition (TTS) Principle [36]. Evidently these five samples exhibit nearly identical linear viscoelastic spectra. We report below only the molecular characteristics of one of the samples, the PS mixture with *h*/*d* = 16:84. The rubbery plateau modulus (G_N^0), determined from the inflection point of $G'(\omega)$, is approximately 0.26 MPa. The relation $M_e = \rho RT/G_N^0$ gives us an entanglement molecular weight M_e of 12.3 kg/mol and an average entanglements per chain ($Z \approx M_w/M_e$) of 18. From the crossover frequency ω_c of the storage and loss moduli, the longest chain relaxation time is estimated to be $\tau \approx \omega_c^{-1} \approx 6.87 \times 10^3$ s at 125°C. On the other hand, the Rouse relaxation time τ_R, calculated using Osaki's formula [37, 38], is 279 s at the same temperature.

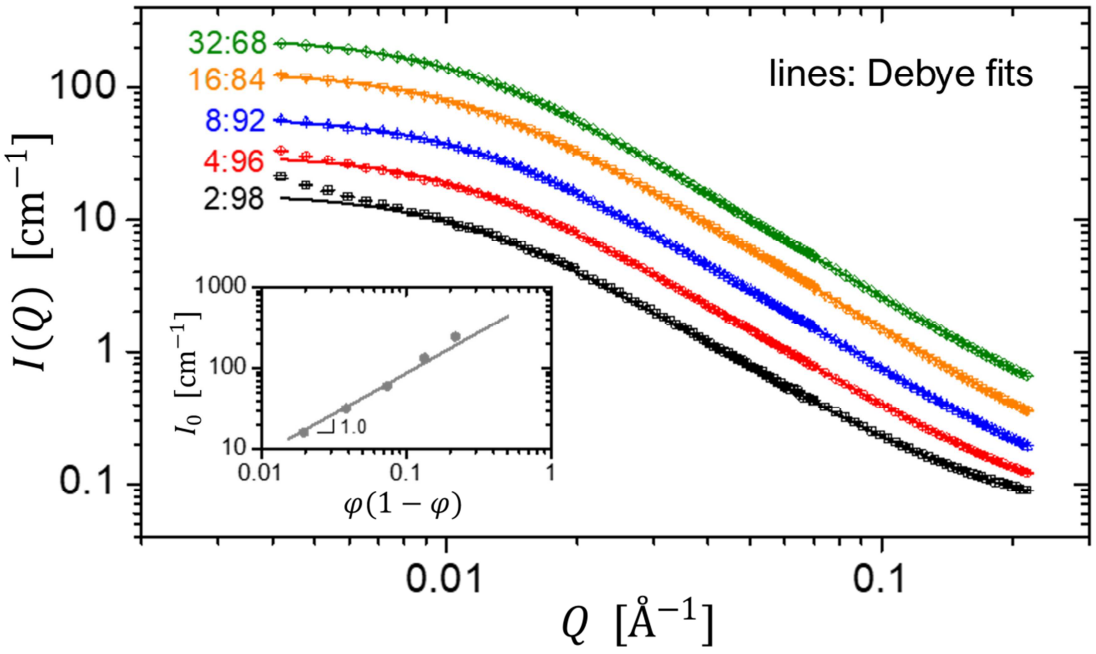

Fig. 3. Small-angle neutron scattering spectra of the isotropic, undeformed polystyrene samples of different *h*/*d* ratios. Solid lines: Fits by the Debye function [Eq. (8)]. Inset: Zero-angle

scattering intensity I_0 as a function of $\varphi(1-\varphi)$. φ: Volume fraction of the hydrogenous polymer.

Consistent with the linear viscoelastic data, the SANS measurements show that apart from different levels of isotope labeling, these samples have almost exactly the same melt structures in the equilibrium state (Fig. 3). Additionally, the data can be well described by the classical Debye function:

$$I(Q) = I_0 g_D(Q^2 R_G^2) + I_{\text{bkg}}, \tag{8}$$

where $g_D(x) = \frac{2}{x^2}(e^{-x} + x - 1)$. The resulting radii of gyration (R_G) from the Debye fits are nearly identical for the five samples: 132 Å for the *h*/*d* = 2:98 sample, 133 Å for 4:96, 128 Å for 8:92, 132 Å for 16:84, and 138 Å for 32:68. And the zero-angle scattering intensity I_0 scales with $\varphi(1-\varphi)$, as expected (inset of Fig. 3). These results are, not surprisingly, in line with the previous investigations in the literature [20, 29, 30]. The observed low-Q upturn in the *h*/*d* = 2:98 and 4:96 samples might be attributed to the presence of micro-sized voids [20].

4.2.Response under deformation

Having verified the basic properties of the polystyrene melts in the equilibrium state, we now turn own attention to the deformed case. Fig. 4 shows the engineering stress σ_E as a function of engineering strain ϵ_E during stretching for all the samples. In accordance with our expectation, these samples exhibit identical stress-strain curves during the entire deformation process. As mentioned in the materials and methods section, the samples were rapidly quenched into a glassy state at the end of uniaxial extension, and the frozen melt structures at $\lambda = 1 + \epsilon_E = 1.8$ were examined by the SANS experiments. (Due to the limitation of SANS counting statistics and the size of RSA-G2 environmental chamber, $\lambda = 1.8$ was a stretching ratio at which the experiment could be comfortably performed.) The (apparent) 2D single-chain structure factor, defined as

$S(Q_x, Q_z) = [I(Q_x, Q_z) - I_{\text{bkg}}]/I_0$, is presented in Fig. 5 for the five deformed samples with different *h*/*d* ratios. Here, the background I_{bkg} and the zero-angle scattering intensity I_0 are obtained from the Debye fitting of the equilibrium SANS spectrum in Fig. 3. Upon visual inspection, we see that these properly subtracted and normalized 2D spectra indeed look identical to each other, in agreement with Eq. (1).

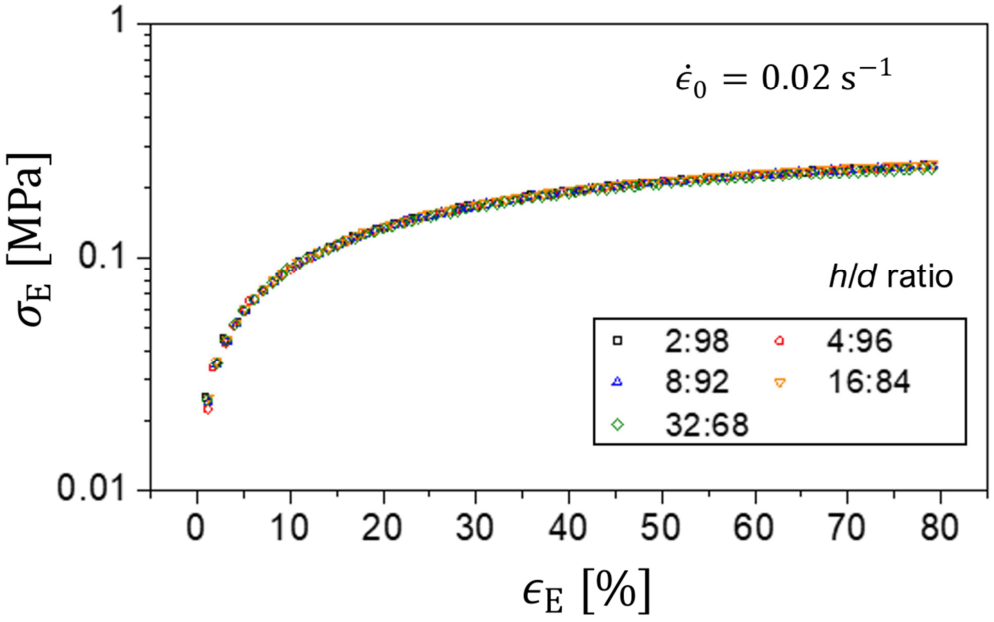

Fig. 4. Engineering stress σ_E as a function of engineering strain ϵ_E during stretching for all the samples at 125□.

To show that the samples indeed have identical anisotropic melt structures, we may select the $S(Q_x, Q_z)$ of one sample as the reference and subtract it from the spectra of other samples. However, this seemingly simple method does have a few drawbacks. First, since it is nontrivial to use logarithmic scales for Q values, the low-Q information is always highly compressed on such 2D plots. Second, the $S(\boldsymbol{Q})$ of this system decays rapidly as the Q increases. Presenting the differential spectra on either linear or logarithmic scales has its own problems. Finally, the use of "colormap" is a delicate art and highly subjective. Depending on the color mapping scheme, the

same data can create rather different visual impressions. While we by no means are advocating the spherical harmonic expansion technique as the only way of analyzing anisotropic 2D SANS spectra, it does appear to be a more tractable method for the current problem.

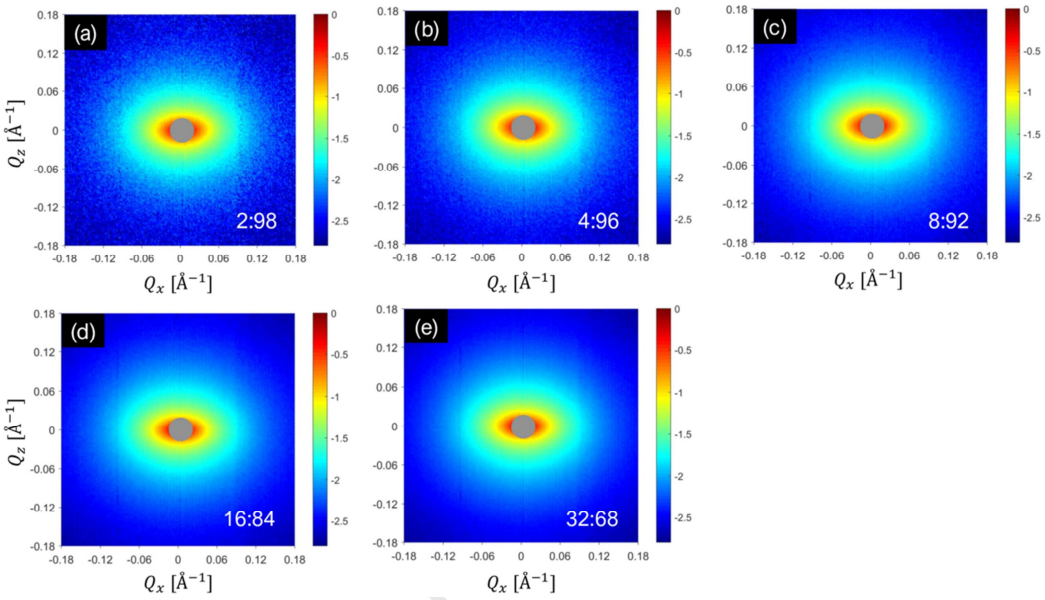

Fig. 5. Two-dimensional single-chain structure factors $log_{10} S(Q_x, Q_z)$ of the stretched polystyrene samples of different *h*/*d* ratios: (a) 2:98, (b) 4:96, (c) 8:92, (d) 16:84, and (e) 32:68. As indicated in the main text, the single-chain structure factor $S(Q_x, Q_z)$ is determined as $S(Q_x, Q_z) = \left[I(Q_x, Q_z) - I_{bkg}\right]/I_0$.

To bring our analysis to a more quantitative level, we compute the spherical harmonic expansion coefficients of the single-chain structure factor, using the procedure detailed in section 2.2. The first three expansion coefficients for the uniaxial symmetry, $S_0^0(Q)$, $S_2^0(Q)$, and $S_4^0(Q)$, are shown in Fig. 6 for all the samples. As explained in our previous work [5], the spherical harmonic expansion analysis is model independent and the determination of $S_l^0(Q)$ is also

independent of each other because of the orthogonality of the spherical harmonic functions.[3] In other words, the values of $S_0^0(Q)$, $S_2^0(Q)$, and $S_4^0(Q)$ are not affected by the truncation of the expansion at a finite degree l. Higher degree expansion coefficients are not presented here, as their magnitude is rather small. As a trivial fact, we note that $S_0^0(Q)$ is the isotropic component of the single-chain structure factor $S(\boldsymbol{Q})$, whereas $S_2^0(Q)$ is the leading anisotropic expansion coefficient. Additionally, it is perhaps helpful to point out that background subtraction has no effect on $S_2^0(Q)$, because I_{bkg} is assumed to be isotropic and therefore only affects $S_0^0(Q)$.

Consistent with our visual "impression" from Fig. 5, the expansion coefficients from the 2D SANS spectra, $S_0^0(Q)$, $S_2^0(Q)$, and $S_4^0(Q)$, are nearly identical for all the five samples [Fig. 6 (a)]. As discussed earlier, the slight low-Q upturn in $S_0^0(Q)$ of the *h*/*d* = 2:98 and 4:96 samples might be attributed to the presence of micro-sized voids. Further plotting the magnitude of $S_0^0(Q)$ and $S_2^0(Q)$ on a logarithmic scale [Figs. 6 (b) and (c)], we clearly see that the data from different samples fall on top of each other over a wide Q range, when $S_0^0(Q)$ and $|S_2^0(Q)|$ vary more than two orders of magnitudes. This striking agreement unquestionably supports the validity of Eq. (1) for mixtures of hydrogenous and deuterated polymers of matching chain lengths in the nonequilibrium state, providing a strong experimental proof for this long-held belief in the community. Together with the evidence from the earlier investigation [20] and detailed theoretical justifications in Appendices A and B, this study should present a final and convincing case for this fundamental assumption in small-angle neutron scattering studies of deformed polymer melts.

[3] In general, computing $S_l^m(Q)$ from small-angle scattering experiments is a nuanced issue. Please see ref. [28] for a further discussion.

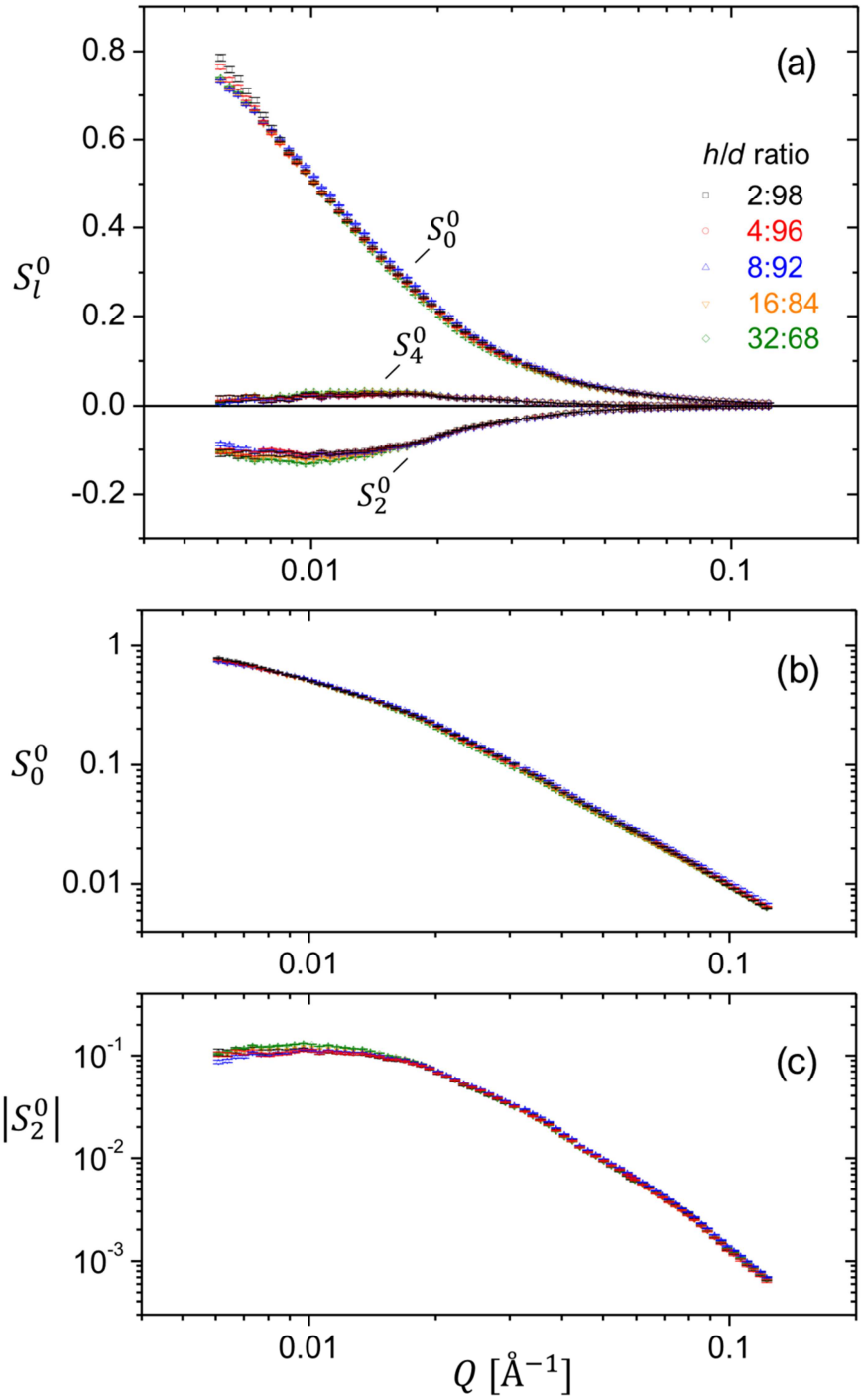

Fig. 6. (a) Spherical harmonic expansion coefficients, $S_0^0(Q)$, $S_2^0(Q)$, and $S_4^0(Q)$ of the stretched polystyrene samples of different *h*/*d* ratios. (b) $S_0^0(Q)$ presented on a double-logarithmic scale. (c) Absolute value of $S_2^0(Q)$.

5. Conclusions and Additional Remarks

In summary, this work critically examines a fundamental assumption in small-angle neutron scattering studies of deformed polymer melts. By combining anionic polymerization, judiciously designed sample preparation procedures, and the spherical harmonic expansion technique, we quantitatively analyze the small-angle neutron scattering spectra from a series of deformed polymer melts that differ only in the degree of deuterium labeling. We show that the measured coherent scattering intensity is indeed proportional to the single-chain structure factor for mixtures of hydrogenous and deuterated polymers of matching chain lengths, even in the deformed state.

Some readers may still wonder why we have spent so much effort to carefully examine, and in some sense re-examine, this old and seemingly closed case (depending on their viewpoint) in SANS studies of polymer melts? We now offer some further explanation. It is well known that for *isotropic* polymer melts, Eq. (2) can be derived from a more general result for binary polymer blends on the basis of the random phase approximation (RPA) [31]:

$$\frac{(b_{\mathrm{D}}-b_{\mathrm{H}})^2 n_{\mathrm{seg}}}{I(\boldsymbol{Q})} = \frac{1}{N_{\mathrm{H}}\varphi_{\mathrm{H}}S_{\mathrm{H}}(\boldsymbol{Q})} + \frac{1}{N_{\mathrm{D}}\varphi_{\mathrm{D}}S_{\mathrm{D}}(\boldsymbol{Q})} - 2\chi, \tag{9}$$

where χ is the Flory interaction parameter, and the lengths N_{H} and N_{D} of the hydrogenous and deuterated chains are generally not equal. Setting $\chi = 0$ and $N_{\mathrm{H}} = N_{\mathrm{D}}$, we trivially recover Eq. (2). Interestingly, SANS experiments have demonstrated that this RPA formula [Eq. (9)] is generally invalid in the deformed state [10], due to the phenomenon of viscoelastic phase separation [39-44]. On the other hand, this study shows that Eq. (2) holds extremely well for mixtures of hydrogenous and deuterated polymers of matching chain lengths even in the nonequilibrium state. Therefore, as long as the polymeric mixtures of matching molecular weights are far away from the phase boundary in the equilibrium state, it is typically not essential

to consider the interaction parameter χ in the deformed state. (While this is a logical conclusion from our study, the readers should take this recommendation with caution.) Additionally, viscoelastic phase separation [39-42] does seem to be main factor for the failure of the general RPA formula [Eq. (9)] under deformation. Because of the absence of viscoelastic asymmetry in mixtures of polymers of matching chain lengths, Eq. (2) remains valid in the deformed state, just as indicated by the theoretical analysis (Appendices A and B) and current and past experimental results.

Acknowledgements

The research (Y.W.) is supported by the U.S. Department of Energy (DOE), Office of Science, Office of Basic Energy Sciences, Early Career Research Program Award KC0400000, under Contract DE-AC05-00OR22725. The synthesis, characterization, and small-angle neutron scattering experiments of the polystyrene samples were performed at Oak Ridge National Laboratory's Center for Nanophase Materials Sciences and Spallation Neutron Source, which are DOE Office of Science User Facilities.

Appendix A. Small-Angle Neutron Scattering by Incompressible Liquids

We reproduce here the derivation of the fundamental theorem for small-angle neutron scattering by incompressible liquids [Eq. (5)]. Although this is a well-known result, we assume that not all readers are familiar with the mathematical details of its derivation. By exposing the underlying mathematics, we show that this theorem is valid for incompressible liquids in both isotropic and *deformed* states. Our proof below is slightly more detailed than the one presented in the classical textbook by Higgins and Benoît [32].

For the convenience of the derivation below, we rewrite the partial structure factor $S_{\alpha\beta}(\boldsymbol{Q})$ in the continuous form:

$$S_{\alpha\beta}(\boldsymbol{Q}) = \iint \langle n_\alpha(\boldsymbol{u}) n_\beta(\boldsymbol{r}+\boldsymbol{u})\rangle e^{-\mathbb{i}\boldsymbol{Q}\cdot\boldsymbol{r}} \mathrm{d}\boldsymbol{u}\mathrm{d}\boldsymbol{r} = \int K(\boldsymbol{r}) e^{-\mathbb{i}\boldsymbol{Q}\cdot\boldsymbol{r}} \mathrm{d}\boldsymbol{r}, \quad \text{(A1)}$$

where n_α is the number density of species α. Focusing on the characteristic function $K(\boldsymbol{r}) \equiv \int \langle n_\alpha(\boldsymbol{u}) n_\beta(\boldsymbol{r}+\boldsymbol{u})\rangle \mathrm{d}\boldsymbol{u}$, we see that

$$K(\boldsymbol{r}) = \int \langle n_\alpha(\boldsymbol{u}) n_\beta(\boldsymbol{r}+\boldsymbol{u})\rangle \mathrm{d}\boldsymbol{u} = \int \langle [\Delta n_\alpha(\boldsymbol{u}) + \langle n_\alpha\rangle][\Delta n_\beta(\boldsymbol{r}+\boldsymbol{u}) + \langle n_\beta\rangle]\rangle \mathrm{d}\boldsymbol{u}, \quad \text{(A2)}$$

where $\Delta n_\alpha(\boldsymbol{r})$ represents the spatial fluctuation of number density of species α: $\Delta n_\alpha(\boldsymbol{r}) \equiv n_\alpha(\boldsymbol{r}) - \langle n_\alpha\rangle$. Expanding the product in Eq. (A2), we have

$$K(\boldsymbol{r}) = T_1 + T_2 + T_3 + T_4, \quad \text{(A3)}$$

with $T_1 = \int \langle \Delta n_\alpha(\boldsymbol{u}) \Delta n_\beta(\boldsymbol{r}+\boldsymbol{u})\rangle \, \mathrm{d}\boldsymbol{u}$, $T_2 = \langle n_\alpha\rangle\langle n_\beta\rangle \int \mathrm{d}\boldsymbol{u}$, $T_3 = \langle n_\beta\rangle \int \langle \Delta n_\alpha(\boldsymbol{u})\rangle \mathrm{d}\boldsymbol{u}$, and $T_4 = \langle n_\alpha\rangle \int \langle \Delta n_\beta(\boldsymbol{r}+\boldsymbol{u})\rangle \mathrm{d}\boldsymbol{u}$. The third term T_3 is zero by definition. And the fourth term T_4 is also zero in most practical cases because it computes the total density fluctuation within a "shifted" volume. Physically, whether we consider the volume defined by $\boldsymbol{u}$ or $\boldsymbol{u}+\boldsymbol{r}$ should not change the average density fluctuation, which is zero for incompressible liquids. Therefore, we have

$$K(\boldsymbol{r}) = \int \langle \Delta n_\alpha(\boldsymbol{u}) \Delta n_\beta(\boldsymbol{r}+\boldsymbol{u})\rangle \, \mathrm{d}\boldsymbol{u} + \langle n_\alpha\rangle\langle n_\beta\rangle V. \quad \text{(A4)}$$

Substituting this result to Eq. (A1) yields

$$S_{\alpha\beta}(\boldsymbol{Q}) = \iint \langle \Delta n_\alpha(\boldsymbol{u}) \Delta n_\beta(\boldsymbol{r}+\boldsymbol{u})\rangle e^{-\mathbb{i}\boldsymbol{Q}\cdot\boldsymbol{r}} \mathrm{d}\boldsymbol{u}\mathrm{d}\boldsymbol{r} + \langle n_\alpha\rangle\langle n_\beta\rangle V(2\pi)^3\delta(\boldsymbol{Q}). \quad \text{(A5)}$$

Since the last term can be discarded for any practical considerations, we have:

$$S_{\alpha\alpha}(\boldsymbol{Q}) \approx \iint \langle \Delta n_\alpha(\boldsymbol{u}) \Delta n_\alpha(\boldsymbol{r}+\boldsymbol{u})\rangle e^{-\mathbb{i}\boldsymbol{Q}\cdot\boldsymbol{r}} \mathrm{d}\boldsymbol{u}\mathrm{d}\boldsymbol{r}, \quad \text{(A6)}$$

$$S_{\alpha\beta}(\boldsymbol{Q}) \approx \iint \langle \Delta n_\alpha(\boldsymbol{u}) \Delta n_\beta(\boldsymbol{r}+\boldsymbol{u})\rangle e^{-\mathbb{i}\boldsymbol{Q}\cdot\boldsymbol{r}} \mathrm{d}\boldsymbol{u}\mathrm{d}\boldsymbol{r}. \quad \text{(A7)}$$

In the current context, we consider the case of a binary mixture, consisting of hydrogenous and deuterated molecules. The incompressibility condition implies $\Delta n_{\mathrm{H}}(\boldsymbol{r}) + \Delta n_{\mathrm{D}}(\boldsymbol{r}) = 0$. Therefore

$$S_{\mathrm{HH}}(\boldsymbol{Q}) + S_{\mathrm{HD}}(\boldsymbol{Q}) \approx \iint \langle \Delta n_{\mathrm{H}}(\boldsymbol{u}) [\Delta n_{\mathrm{H}}(\boldsymbol{r}+\boldsymbol{u}) + \Delta n_{\mathrm{D}}(\boldsymbol{r}+\boldsymbol{u})]\rangle e^{-\mathbb{i}\boldsymbol{Q}\cdot\boldsymbol{r}} \mathrm{d}\boldsymbol{u}\mathrm{d}\boldsymbol{r} = 0. \quad \text{(A8)}$$

Similarly, we can show that $S_{\mathrm{DD}}(\boldsymbol{Q}) + S_{\mathrm{HD}}(\boldsymbol{Q}) = 0$. The coherent scattering intensity from a two-component system can be formally expressed as $I_{\mathrm{coh}}(\boldsymbol{Q}) = b_{\mathrm{H}}^2 S_{\mathrm{HH}}(\boldsymbol{Q}) + 2b_{\mathrm{H}}b_{\mathrm{D}}S_{\mathrm{HD}}(\boldsymbol{Q}) +$

$b_{\mathrm{D}}^2 S_{\mathrm{DD}}(\boldsymbol{Q})$. Applying the above results obtained from the incompressibility condition, the scattering intensity can be rewritten as

$$I_{\mathrm{coh}}(\boldsymbol{Q}) = (b_{\mathrm{H}} - b_{\mathrm{D}})^2 S_{\mathrm{HH}}(\boldsymbol{Q}) = (b_{\mathrm{H}} - b_{\mathrm{D}})^2 S_{\mathrm{DD}}(\boldsymbol{Q}) = -(b_{\mathrm{H}} - b_{\mathrm{D}})^2 S_{\mathrm{HD}}(\boldsymbol{Q}). \quad \text{(A9)}$$

The presented derivation contains nothing original. The goal of this exercise is to emphasize, by rigorous mathematics, that the above fundamental relation [Eq. (A9)] holds in both isotropic and deformed states. In reality, no liquid is completely incompressible. The consequence of finite compressibility has been considered and discussed by a number of authors [45, 46]. However, the present experimental study, along many others in the literature, shows that for isotopically labeled polymer melts the incompressibility assumption works well and there seems to be no need to consider the finite compressibility of polymeric liquids.

Appendix B. Scattering from Isotopically Labeled Polymer Melts

Now we further consider the application of the above theorem to small-angle neutron scattering by isotopically labeled incompressible polymer melts, consisting of hydrogenous and deuterated chains of identical degree of polymerization [32]. Once again, the analysis itself contains nothing original. Our goal is to highlight, by dissecting the classical proof, the basic assumptions that need to be re-examined in the context of flow and deformation. Following the approach of Higgins and Benoît [32], one can separate the interchain and intrachain contributions to the partial structure factors as:

$$S_{\mathrm{HH}}(\boldsymbol{Q}) = M_{\mathrm{H}} N_{\mathrm{H}}^2 S_{\mathrm{HH,intra}}(\boldsymbol{Q}) + M_{\mathrm{H}}^2 N_{\mathrm{H}}^2 S_{\mathrm{HH,inter}}(\boldsymbol{Q}), \quad \text{(B1)}$$

$$S_{\mathrm{DD}}(\boldsymbol{Q}) = M_{\mathrm{D}} N_{\mathrm{D}}^2 S_{\mathrm{DD,intra}}(\boldsymbol{Q}) + M_{\mathrm{D}}^2 N_{\mathrm{D}}^2 S_{\mathrm{DD,inter}}(\boldsymbol{Q}), \quad \text{(B2)}$$

$$S_{\mathrm{HD}}(\boldsymbol{Q}) = M_{\mathrm{H}} M_{\mathrm{D}} N_{\mathrm{H}} N_{\mathrm{D}} S_{\mathrm{HD,inter}}(\boldsymbol{Q}), \quad \text{(B3)}$$

where M_α is the number of chains of species α in the system and N_α is the number of segments per chain, commensurate with the coherent scattering length calculation. Let M be the total

number of molecules and φ the volume (molar) fraction of the hydrogenous polymer. Furthermore, in the case of ideal mixing, we have $S_{\mathrm{HH,inter}}(\boldsymbol{Q}) = S_{\mathrm{DD,inter}}(\boldsymbol{Q}) = S_{\mathrm{HD,inter}}(\boldsymbol{Q})$ and $S_{\mathrm{HH,intra}}(\boldsymbol{Q}) = S_{\mathrm{DD,intra}}(\boldsymbol{Q})$. The above equations can therefore be rewritten as

$$S_{\mathrm{HH}}(\boldsymbol{Q}) = \varphi M N^2 S_{\mathrm{intra}}(\boldsymbol{Q}) + \varphi^2 M^2 N^2 S_{\mathrm{inter}}(\boldsymbol{Q}). \tag{B4}$$

$$S_{\mathrm{DD}}(\boldsymbol{Q}) = (1-\varphi) M N^2 S_{\mathrm{intra}}(\boldsymbol{Q}) + (1-\varphi)^2 M^2 N^2 S_{\mathrm{inter}}(\boldsymbol{Q}). \tag{B5}$$

$$S_{\mathrm{HD}}(\boldsymbol{Q}) = \varphi(1-\varphi) M^2 N^2 S_{\mathrm{inter}}(\boldsymbol{Q}). \tag{B6}$$

It follows that

$$\varphi M N^2 S_{\mathrm{intra}}(\boldsymbol{Q}) + \varphi^2 M^2 N^2 S_{\mathrm{inter}}(\boldsymbol{Q}) = -\varphi(1-\varphi) M^2 N^2 S_{\mathrm{inter}}(\boldsymbol{Q}), \tag{B7}$$

which further yields

$$S_{\mathrm{intra}}(\boldsymbol{Q}) = -M S_{\mathrm{inter}}(\boldsymbol{Q}). \tag{B8}$$

Finally, we have

$$I_{\mathrm{coh}}(\boldsymbol{Q}) = (b_{\mathrm{H}} - b_{\mathrm{D}})^2 \varphi(1-\varphi) M N^2 S_{\mathrm{intra}}(\boldsymbol{Q}). \tag{B9}$$

It should be pointed out that Eq. (2) as well as the rest of the main text uses “absolute intensity” whereas “nominal (total) intensity” is adopted in the appendices. These two kinds of intensities differ by a normalization constant, which is the volume of the system. With this in mind, it is easy to see that Eq. (B9) leads directly to Eq. (2).

Mathematically, the above derivation involves only elementary arithmetic and is not affected by deformation. Additionally, the basic assumptions that $S_{\mathrm{HH,inter}}(\boldsymbol{Q}) = S_{\mathrm{DD,inter}}(\boldsymbol{Q}) = S_{\mathrm{HD,inter}}(\boldsymbol{Q})$ and $S_{\mathrm{HH,intra}}(\boldsymbol{Q}) = S_{\mathrm{DD,intra}}(\boldsymbol{Q})$ do not require polymers to be in the isotropic state. However, in making these assertions, we do implicitly assume that isotopic labeling, *i.e.*, deuteration, does not affect the structure and dynamics of the system in any significant way. In other words, the mixing of the hydrogenous and deuterated components is ideal or nearly ideal. This is a reasonable assumption when the system is far away from the phase boundary.

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Graphical Abstract

Quantitative examination of a fundamental assumption in small-angle neutron scattering studies of deformed polymer melts

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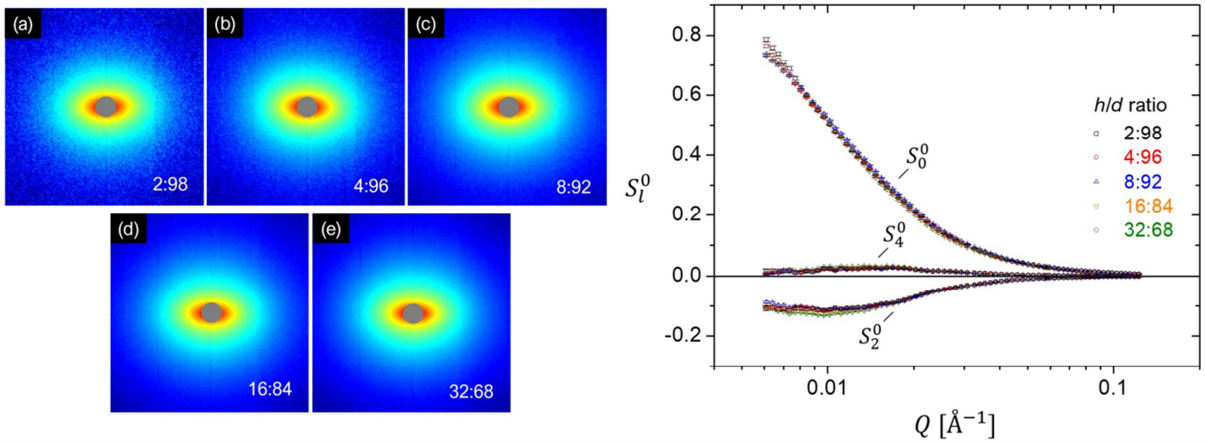

Research Highlights

- Application of the spherical harmonic expansion technique to quantitatively the SANS spectra
- Carefully designed and prepared experimental systems with identical melt structure and linear and nonlinear viscoelastic properties
- Confirmation of a fundamental assumption in SANS studies of deformed polymer melts
- Detailed exposition of relevant theoretical arguments

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: