

Neutron Scattering Applications in Hydrocarbon Materials

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Neutron scattering methods are a powerful probe to complex fluids, soft matters as well as solid materials of nano- and micro-structures and their related dynamic properties. They complement other microstructural probing tools, such as microscopes, x-ray and light scattering techniques. Because neutron does not carry charges, it interacts only with nuclei of the matter, therefore not only can it penetrate a longer length into matters, it can also "see" many features other methods can't due to their lack of proper contrast or heavy absorption. One of the largest contrasts in neutron methods is from hydrogen/deuterium (H/D) difference. Therefore, hydrocarbons can be easily studied by neutrons when H/D isotope substitution is applied. Here at National Institute of Standards and Technology's Center for Neutron Research (NCNR) in Gaithersburg, Maryland, one of the USA's premier neutron scattering facilities, we have been using neutron scattering techniques to study microstructures of asphaltenes, waxes, gas hydrates, porous media, surfactant solutions, engine oils, polymers, nanocomposites, fuel cell element and other hydrocarbon materials. With the completion of a new Neutron Spin Echo instrument, we can also look at the dynamics of the above mentioned systems.

KEYWORDS: hydrocarbon, neutron scattering, size, shape, molecular weight

§1. Introduction

Neutron scattering has been widely used in materials research during the last decade, thanks to advances in neutron scattering techniques and facilities. It not only complement other scattering techniques such as x-ray scattering or light scattering, it in many cases has its unparalleled advantages, because of unique features of neutron and its interaction with matters. The mostly used neutron scattering method is small angle neutron scattering, or SANS. SANS is a type of static elastic scattering. Because it does not exchange energy with the probed sample, the scattering does not carry information of the dynamics. Neutron scatters a small angle due to the density fluctuations in the sample, so the scattering intensity as a function of the angle carries information of the sample's microstructure. Indeed, the scattering intensity $I(q)$ as a function of the scattering wavevector, q , is a Fourier transform of the real space density function. Here q combines both the scattering angle θ , and neutron wavelength λ

$$q = \frac{4\pi}{\lambda} \sin \frac{\theta}{2}. \quad (1.1)$$

The property of Fourier transform dictates that the intensity $I(q)$ is most sensitive to density changes in a length scale at $l \cong 1/q$. Therefore, in order to probe length scales from nanometers to microns, with neutron wavelength as long as 1 nm, one has to go to very small angle. For example, a length of 1 micron corresponds to an angle of 0.002 radian, or 0.1 degree. Currently,

conventional SANS instrument can have a resolution to probe a q of 0.01/nm,¹⁾ or a length scale of 100 nm. Recently developed ultra-small angle (u-SANS) instruments can probe length scales of several microns.²⁾

Since SANS probes the density fluctuation in real spaces, it is similar to a microscope, albeit with much better statistics. Even though it does not provide real space images, it provides such important morphological information as particle size, shape, mass or molecular weight, orientations, and their distributions. For non-particulate systems as well as particulate systems, it can provide surface information, such as total surface area, surface curvature, and interfacial conditions (rough, sharp, or diffusive). With features like high penetration length and contrast variation, neutron scattering is a very powerful probing technique, especially, for hydrocarbon materials.

§2. Size Determination

One of the most powerful features of SANS probing complex fluids or polymers is that it can measure the size of particles in solution, or polymer chain length in solution or in melt relatively accurately and easily. The only requirement is that the size range is in the instrument resolution, or less than 100 nm for most conventional SANS, or microns for u-SANS. It is based on Guinier law, where the form factor, or the scattering intensity itself when there is no interactions among the particles, is in the form

$$I(q) = I(0) \exp\left(-\frac{1}{3} R_g^2 q^2\right), \quad (2.1)$$

provided qR_g is less than unity, where R_g is the radius of gyration of the structure (particles, polymers). For a

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sphere, $R_g = 0.775r$ where r is its radius.

As can be seen from eq. (2.1), the size R_g is determined from the exponent of the intensity, or the slope in a $\ln I(q)$ vs q^2 plot (such plots are traditionally called Guinier plots). It is independent from the uncertainties of the absolute intensity calibration, $I(0)$, which for many samples or instruments is not easily determined.

Of course, the probed structure needs to have some contrast against the rest of the sample, or background. It is not a problem for solutions, since the solute is different from the solvent, and in many cases, deuterated solvents, which provide high contrast and low incoherent background are readily available. In the case of homopolymers, the contrast can be obtained by selectively deuterating part of the polymer chains. One example in polyethylene is to obtain the average tie-chain numbers. Tie chains are those parts of a polymer chain inside amorphous phases linking at both ends parts of the same polymer chain in crystalline phases.³⁾ It is believed that more the tie chains, the better the mechanical properties of the polymer products. SANS experiments with selective deuteration provide the only method to date to directly measure the number of tie chains.

§3. Morphology Shape

The shape of a structure, whether it's spherical, cylindrical, or polymer chain like, can also be determined from the shape of the intensity curve $I(q)$ in a wide q range. In many cases, a power law behavior can be found for the intensity, $I(q)$ vs $q^{-\alpha}$, with the exponent α reflecting the dimension or shape of the structure probed. Some specific examples: for rod-like structures, $\alpha=1$; disk-like, $\alpha=2$; for polymer in melt, $\alpha=2$; polymer in good solvent, 1.67. Similarly, for a mass fractal of fractal dimension d , $\alpha=d$.⁴⁾

Once the shape can be determined or assumed, the whole $I(q)$ curve can be fit to obtain a size-shape-orientation distribution. Here specific model is required. Experiments have been performed on rod-like micelle solutions under shear flow, to determine the size, orientation relative to the shear, of the micelles.⁵⁾

A good application of the contrast variation using D/H substitution is in a situation where more than two phases are present. For example, in typical lube oil, there are usually more than one species present in addition to the base oil. A colloidal core surrounded by a surfactant shell is usually the structure of the detergent added. The size, shape of both the core and the shell can be determined by varying the base oil deuteration.⁶⁾ When the base oil's scattering length density is matched with the shell's, it is only the core that is visible to neutrons, and vice versa.

§4. Molecular Weight Determination

Particle mass or molecular weight of polymers can be determined if the prefactor $I(0)$ in eq. (2.1) can be obtained or measured. It requires instrument calibration and is now routinely done by measuring some standard samples at the same instrument configuration. The prefactor consists of

$$I(0) = nv^2\Delta\rho^2 = cm\Delta\rho^2/d^2 \quad (4.1)$$

where n is the number density (per cc) and $c = nm$ is the concentration in g/cc, of the particles, v is the volume, m is the mass, and $d=m/v$ is the density of a single particle, and $\Delta\rho$ is the contrast factor, or the difference of the particle (polymer) in scattering length density with the surrounding matrix. With everything else predetermined, and $I(0)$ measured in a SANS experiment, the mass m or molecular weight can be obtained.

§5. Polymer Blends Miscibility/Compatibility

Polymer blends miscibility has been characterized by the Flory-Huggins χ parameter.⁷⁾ In a scattering experiment, it can be determined by measuring the scattering intensity. Using random phase approximation, it can be shown

$$\frac{I(0)}{I(q)} = \frac{1}{v_1 N_1 \phi_1 S(qR_{g1})} + \frac{1}{v_2 N_2 \phi_2 S(qR_{g2})} - 2\frac{\chi}{v_0} \quad (5.1)$$

where v , N , ϕ are the volume, degree of polymerization, and volume fraction of polymer type 1 or 2, and the subscripts represent the two types of polymers. v_0 is an average of v_1 and v_2 , and $S(x)$ is the structure factor (Debye function) for a single chain. In an ideal case, when $\chi=0$, Equation (5.1) reduces back to the homopolymer case, although part of the polymers have to be deuterated to provide some contrast.

In many cases, a polymer blend is truly immiscible. They form phase-separated micromorphology with pure type 1 and type 2 polymer domains. The adhesion property of such a blend depends on how the interfacial properties are between these polymer domains. SANS can provide valuable information on how diffusive the interfaces are. If the interfaces are very sharp, that is, there is no mixing even at the interfaces between the two types of polymers, Porod law predicts that the scattering gives a -4th power law:

$$I(q) = Aq^{-\alpha}, \quad (5.2)$$

when q is large compared with the inverse of any domain size R , where $\alpha=4$ for sharp surfaces and A is a constant related to the total surface area per unit volume. When $3<\alpha<4$, the surfaces are said to be rough but still sharp, and can be characterized as surface fractal.^{4) 8)} When $\alpha>4$, the surfaces are diffusive, where there are some mixing at the domain boundaries.⁹⁾

SANS experiments have been performed on immiscible polymer blends to study the interfacial properties of the segregated polymer phases, and the exponent α is used to characterize the diffusiveness of the interfaces. In one study, brominated poly(isobutylene-co-paramethyl styrene) (BIMS) and deuterated polybutadiene (dPB) blends were examined by SANS. BIMS is a new type of polyelastomer (rubber) materials, and PB is a major component of the more commonly used general rubber. For comparison, a blend of PB and deuterated polystyrenebutadiene (dPSB) was also examined, in which the two polymers are more similar in chemical structure, and therefore more compatible. Figure 1 shows an $I(q)$ vs. q plot for the two blends. Curve (a) (circles) is for the BIMS/dPB blend, having an exponent $\alpha = 4.06$, characteristic of sharp interfaces, as expected

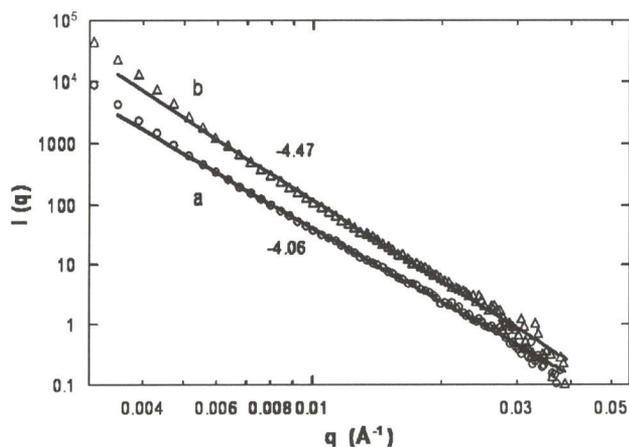


Fig.1. Neutron scattering intensity as a function of q for BIMS/dPB blend (a), and PB/dPBS blend (b). The solid lines are fits to the curves, with their slope (power law exponent $-\alpha$ marked).

for the two incompatible polymers. Curve (b) (triangles) is for the more compatible PB/dPBS blend, having $\alpha = 4.47$, suggesting that more diffusive interfaces are between these two polymers.

To further study whether thermal treatment would help "incompatible" polymer blends become more diffusive at interfaces, the same samples were heated to 90 °C and subsequently to 150 °C, and then were kept at 150 °C for 4 hours. At each step, SANS data were taken and the exponent α determined. Figure 2 shows α as a function of this process. The circles (curve a) are for the BIMS/dPB blend, which is seen to change from sharp interfaces ($\alpha \cong 4$) to slightly diffusive ($\alpha > \cong 4$) as temperature increases, suggesting the thermal treatment helps to make the two types of polymer more adhesive or more compatible. For the PSB/dPS blend (triangles), it is already very diffusive ($\alpha > 4$) to start with, and increasing temperature does not help more diffusivity. With a model fitting, the interfacial width can also be determined, and the results can be compared with neutron reflectivity experiments, which study the diffusivity of a flat macroscopic interface of the two polymers.¹⁰⁾

To conclude, neutron scattering, especially SANS, has

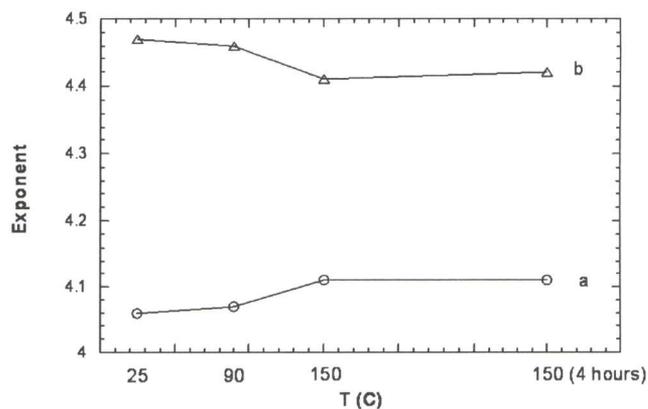


Fig.2. Exponent α as a function of thermal treatment determined from SANS data for the same two polymer blends. Note a sharp interface would have $\alpha=4$ (Porod law).

many features of static scattering that help to probe microstructures of materials. However, due to the unique features of neutron, one of which is the contrast variation by H/D substitution, the technique is more suitable to study hydrocarbons.

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