Scattering Methods Applied to High Throughput Materials Science.

Alexander I. Norman [1], João T. Cabral [1], Derek L. Ho [2], Eric J. Amis [1] and Alamgir Karim [1].

[1] Polymers Division, Stop 8542, National Institute of Standards and Technology, 100 Bureau Drive, Gaithersburg, MD 20878.
[2] NIST Center for Neutron Research, Stop 8562, National Institute of Standards and Technology, 100 Bureau Drive, Gaithersburg, MD 20878.

INTRODUCTION

High throughput scattering methods are employed to study phase behavior over a concentration gradient of either Polystyrene (PS) in a Polystyrene/Polybutadiene (PS/PB) blend, or of diblock copoly(ethyleneoxide-butyleneoxide) in water. The combinatorial approach uses discrete multiple samples removing the need for preparing each individual sample and reducing experimental acquisition time since the samples do not need to be loaded individually and no realignment procedures are required. X-ray scattering techniques are used to study the ethyleneoxide (EO)/butyleneoxide (BO) system since they cover length scales ranging from a few angstroms (Wide angle x-ray scattering, WAXS) to hundreds of nanometers (Small angle x-ray scattering, SAXS). All SAXS/WAXS experiments are carried out at the NSLS at Brookhaven National Laboratory [1], where the flux is significantly higher than conventional lab sources. In this work we used a 25-well array (with sample volume ≈ 150 μL) spanning concentrations of 0 % by mass fraction to 20 % by mass fraction in increments of 0.8 %. Over this chosen concentration regime, the vesicle structure was known to exist.[2] Vesicles are excellent candidates for controlled release materials. Applications of such materials include pharmaceuticals, agricultural applications and personal care products. [3-5] Such structures were also probed by small angle neutron scattering (SANS) studies and compared to SANS studies of micelles

EXPERIMENTAL

Sample Preparation

A sample of poly(ethyleneoxide-b-butyleneoxide) EO(6)BO(11) was obtained from the Dow Chemical Company and used as received. Details of the synthesis and characterization can be found in the literature. [2] A 20 % by mass fraction solution was prepared using de-ionized water, mechanically agitated for 30 s and allowed to stand for 24 h. The discrete composition gradient was prepared using a home built liquid dispenser and deposited onto the substrate. Details on this and fabrication of the substrate has been reported. [6] A PDMS substrate was chosen due to the impermeability to water and it's adhesion to the polyimide windows employed. Polyimide windows were chosen due to the transparency of the material to x-rays. For light scattering studies a glass window was used.

Small Angle Scattering

Simultaneous SAXS/WAXS measurements were carried out on beamline X27C at the NSLS of BNL. The beamline was configured for SAXS/WAXS using monochromatic radiation of wavelength 1.366 Å. The sample array was held vertically in front of the x-ray beam and moved on a motorized translation stage. A 120 s exposure time was employed, resulting in 25 SAXS/WAXS data sets over the whole vesicle concentration range to be probed in less than 1 h. SANS measurements on a similar block copolymer, EO(18)BO(9), were performed on the 30 m SANS beamline at the NCNR, Gaithersburg, Maryland. Temperature ramps tests were performed to investigate the structure as a function of temperature.

RESULTS

Figure 1 shows the SAXS profile (as a function of concentration) for the 25-well array of EO(6)BO(11) in water. A broad SAXS peak is shown to develop as the concentration is increased. The broadness of this reflection is due to the curvature of the lamellar structure within the spherical vesicle. This concludes that as the concentration of the block copolymer increases, spherical lamellae form and become correlated as the concentration increases further. In addition, the peak shifts to a larger q value indicating that the vesicle shell becomes thinner. The SAXS spectra were analyzed using an indirect Fourier transformation to extract the pair distance distribution function, p(r). The p(r) function is symmetrical and typical of a spherical structure [7]. The maximum particle dimension obtained using this technique is 700 Å. Experimental data from the WAXS provides evidence to suggest zero crystallinity in the system, since a broad amorphous peak is shown. In addition to the combinatorial library investigated, a range of concentrations over a temperature ramp has been studied by both SAXS and SANS. SANS data suggests that prior to vesicle formation (for a low concentration sample, e.g. 0.05 % by mass fraction), the system is a disordered array of worm-like micelles, and that on increasing temperature the vesicle structure forms. On increasing the temperature further the vesicle structure is shown to collapse and reorder into a hexagonal array of rod-like micelles, indicated by higher orders of reflection given in both the SAXS and SANS data. To visualize the changes in scattering profiles an integration over the relevant *q* range was performed to yield the invariant, *Q*.

$$Q = \int_{q_1}^{q_2} I(q).dq$$

For example, at 20 % (by mass fraction), the vesicle structure is shown to persist, and at 40 °C there is a slight increase in intensity, indicating that the vesicles have increased in volume and packed closer together. The vesicle increases in volume because, as the temperature increases, water becomes a poorer solvent for the EO headgroup and to compensate for this an increase in volume occurs. This behavior continues up to 60 °C, where suddenly there is a reduction in scattered intensity indicated destruction of the ordered vesicle structure. However, at 70 °C, there is a rapid increase in intensity, which corresponds to the formation of the lyotropic liquid crystalline phase.

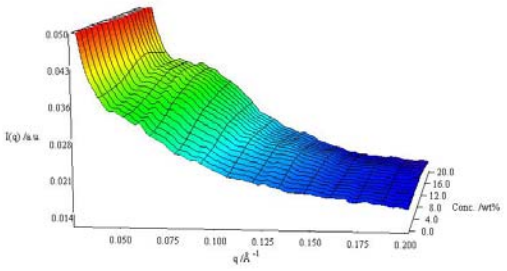

Figure 1. SAXS profile of *I(q) vs. q vs. Concentration* for EO(6)BO(11) in water.

CONCLUSION

In conclusion we have successfully identified the phase behavior of a block copolymer that forms vesicles over a given concentration regime by combinatorial SAXS/WAXS techniques. The automated acquisition and multi-well sample library drastically reduces experimental time. Time resolved SAXS/WAXS techniques and variable temperature SANS measurements identified the phase transitions of worm-like micelle to vesicle to lyotropic liquid crystal phase. The use of an indirect Fourier transformation has allowed us to look at the data in real space to examine particle shape and dimension. In addition, the development of a novel multi-well heating stage allows

such systems to be probed in a high throughput way as a function of temperature using the in house SALS apparatus, which covers a much larger scale window.

ACKNOWLDEGMENTS

We would like to express our gratitude to Igors Sics at the National Synchrotron Light Source at Brookhaven National Laboratory and Sheng Lin Gibson at the National Institute of Standards and Technology for their kind assistance during the SAXS/WAXS experiments. We are grateful to Kapeeleshwar Krishana (Rhodia) for his assistance in setting up the liquid dispenser. The authors would also like to give special thanks to Wim Bras at the European Synchrotron Radiation Facility for valuable discussions into the modeling of the SAXS and SANS data.

REFERENCES

1. Research carried out (in whole or in part) at the National Synchrotron Light Source Brookhaven National Laboratory, which is supported by the U.S. Department of Energy, Division of Materials Sciences and Division of Chemical Sciences, under contract number DE-AC02-98CH10886
2. Harris, J. K.; Rose, G. D.; Bruening, M. L. Langmuir, 2002, 18, 5337.
3. Lasic, D. D. in *Vesicles,* Rossoff, M., Ed: Marcel Dekker: New York, 1996; p 448.
4. Allen, C.; Maysinger, D.; Eisennberg, A. *Coolids Surf. B.* **1999,** *16,* 3.
5. Ding, J.; Liu, G. *J. Phys. Chem. B.* **1998,** *102,* 6107.
6. Harrison, C.; Cabral, J. T.; Stafford, C. M.; Karim, A.; Amis, E. J. *J. Micromech. Microeng.* **2004,** *14,* 153.
7. Glatter, O. in *Neutrons, X-Rays, and Light: Scattering methods applied to soft condensed matter,* Ed. Lindner, P.; Zemb, T., Elsevier, 2000, p. 82-83.