

Chapter 35 - INTRODUCTION TO POLYMERS

Polymer research makes up a good fraction of beamtime use on SANS instruments. Using the partial deuteration method, SANS has been useful for investigations of chain conformations and miscibility in polymer solutions and polymer blend mixtures as well as in other polymeric systems. Many aspects of polymer research have benefited from the SANS technique.

1. WHAT ARE POLYMERS?

Polymers are synthetic macromolecules that make up a great deal of what we use in our daily lives. They include low-cost disposable conveniences (like milk containers or soda bottles) to high-tech structural materials (like hip joint replacement or computer CDs). Polymers are split into “bunching” categories like solutions or blends (alloyed polymers), thermoplastics (that can deform) or thermosets (that are hard to deform), with linear or branched architectures, that are amorphous or crystalline, etc. (Bandrup-Immergut 1975; Kawakatsu, 2004). Liquid crystal polymers contain stiff mesogen groups that increase material toughness. Their high degree of alignment makes them useful in optical devices. Polyolefins (polymers that containing C=C double bonds) are at the heart of petroleum chemistry. Much SANS research has been performed on polyolefins. SANS from polymers research is broad and deep. Only the simplest aspects of this research are covered here.

Polymer research has bloomed over the past fifty years (Flory, 1969; de Gennes, 1979; Higgins-Benoit, 1994). The development of light scattering in the 1960s and of neutron scattering in the 1970s along with advances in polymer synthesis and computational power have greatly benefited polymer research. Impact of the SANS technique has been substantial in many areas of polymer research.

2. SANS FROM POLYMERS

Polymer research has benefited greatly from the SANS technique which matured in the 1970s and 1980s. SANS was first developed to the scale of a user program at the ILL (Grenoble, France) then spread to most neutron scattering facilities. Polymer research accounted for the largest share of SANS beamtime. The advent of judicious sample environments brought about renewed interest. These include temperature and pressure control, the application of in-situ shear, etc. The development of scattering theory for polymer systems such as the Random Phase Approximation helped promote growth in the use of the technique. Most neutron scattering facilities maintain SANS instruments that are overbooked. SANS from polymers research has developed from cutting edge research for hardcore users into a routine characterization method for laboratories that have access to the technique. For example, the Exxon Mobil company has maintained constant use of the SANS technique and its constant funding at the NCNR for almost

twenty years. Moreover, the National Science Foundation has copiously funded the SANS program at many US facilities.

3. POLYMER CHAIN CONFORMATIONS

The partial deuteration method helps observe the conformation of polymer chains in the environment of a solvent or of other polymers. This is similar to the staining method in microscopy. An apparent radius of gyration is often estimated from SANS data in the Guinier region. The Porod region yields chain conformation details such as the degree of chain swelling or solvent quality in polymer solutions. This region also shows the onset of chain stiffness whereby the polymer chain persistence length can be measured.

The SANS technique has permitted measurements of the radius of gyration of polymer chains in various polymer systems whether in solution or in blends. The contrast match method has helped the separation of single-chain properties even in concentrated mixtures. It was found for example, that polymer chains follow random walk statistics in “theta” solvents, in concentrated solutions as well as in polymer melts.

4. THERMODYNAMICS OF POLYMER MISCIBILITY

SANS intensity increases close to phase separation lines due to enhanced composition fluctuations. This makes SANS an effective tool for the investigation of miscibility thermodynamics. Polymeric systems phase separate either through heating and are characterized by a lower critical solution (or spinodal) temperature (LCST) or through cooling and are characterized by an upper critical solution temperature (UCST). Some polymer solutions or polymer blend mixtures are known to phase separate through both heating and cooling and are characterized by a miscibility gap. Others phase separate only within a specific temperature region and are characterized by a closed loop immiscibility island. Polymer solutions in organic solvents tend to be characterized by UCSTs whereas water soluble polymers tend to be characterized by LCSTs. The four major types of phase diagrams are summarized in a figure. Combination of these basic types is also possible; for example UCST at low temperature and closed loop immiscibility at high temperature.

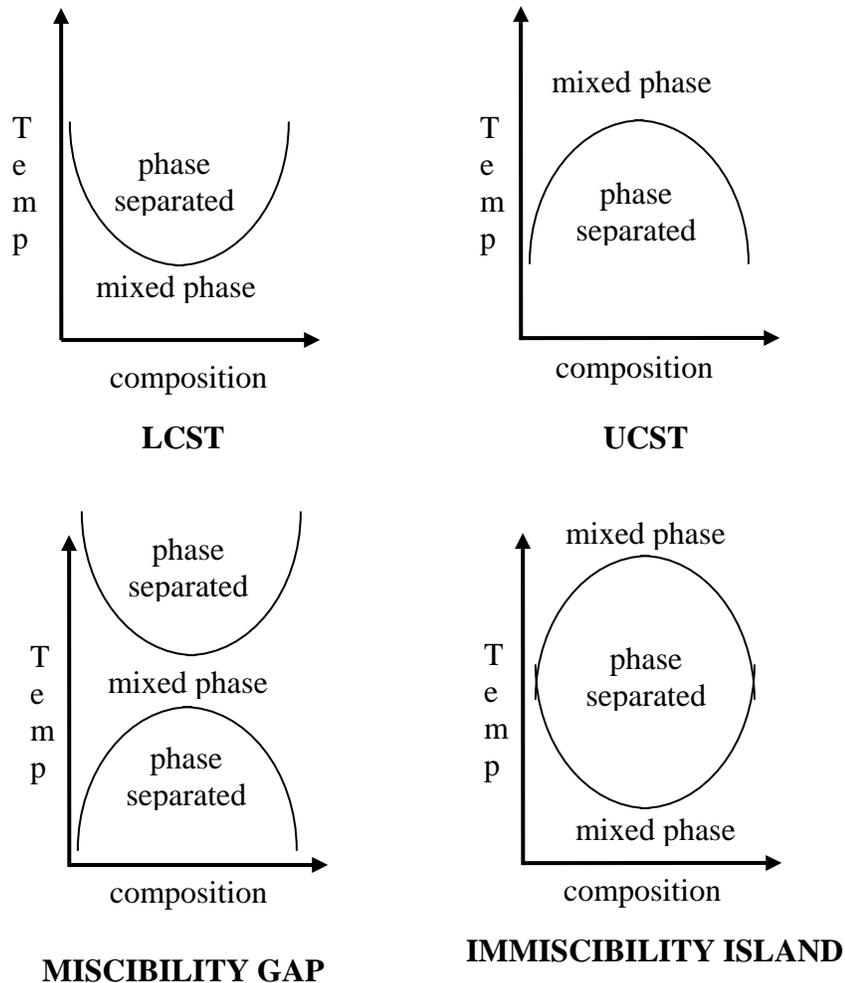


Figure 1: The **four main types of phase separation diagrams** for polymer blends showing the variation of the phase separation temperature with polymer composition. Upper left: LCST, upper right: UCST, lower left: miscibility gap, lower right: closed loop immiscibility island.

The SANS technique has permitted the **determination of Flory-Huggins interaction parameters** and the **mapping out of miscibility phase diagrams**. The advent of in-situ pressure and temperature control has brought about a better understanding of polymer thermodynamics.

5. CRYSTALLINE POLYMERS

The **SANS technique probes density fluctuations** (just like SAXS using x-rays) **as well as composition fluctuations**. **Crystalline polymers are characterized by a strong low-Q signal** below the crystallization temperature. This is due to the density fluctuations component. The use of partially deuterated chains allows the monitoring of chain conformation inside crystallites. Early findings have found, for instance, that polymer chains follow Gaussian

chain statistics in the crystalline lamellae as well as in the melt state. It was also found that melt crystallization is characterized by “random re-entry” of the polymer chains to form lamellae. Solution crystallized polymers, however, are characterized by an “adjacent re-entry” scheme.

REFERENCES

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QUESTIONS

1. When was the “golden age” for polymers research?
2. What are thermoplastics? How about thermosets?
3. Name some contributions of the SANS technique to polymer research.
4. Why is the SANS technique a good probe for thermodynamics investigations? How is this manifested?

ANSWERS

1. Polymers research was very strong for the past 50 years. Lots of progress was made in the 1960s and 1970s.
2. Thermoplastics can recover their original shapes when they are deformed. Thermosets are highly cross linked. It is hard to deform them.
3. The SANS technique has had broad impact on polymer research. A few examples follow: single-chain conformations in polymeric materials, phase separation thermodynamics, chain properties in crystalline polymers, clustering in water-soluble polymer solutions, etc.
4. The SANS technique is a good thermodynamics probe since it can monitor density and composition fluctuation. The intensity increases close to phase transition boundaries.