

Osmotic De-swelling of Temperature-sensitive Microgels as Observed by Ultrasmall-angle X-ray Scattering

P. Mullick, C.F. Zukoski

University of Illinois at Urbana-Champaign, Urbana, IL, U.S.A.

Introduction

Responsive fluids have various potential applications, such as the separation of bio-molecules, drug delivery, and rheological property modifiers. Controlling particle size is the key to these applications. In this study, we employ temperature-sensitive microgel particles that undergo a volume phase transition over a small range of temperatures. The microgel particles are composed of cross-linked polymer chains of poly(*N*-isopropylacrylamide). The equilibrium particle size is determined by the equilibrium of the solvent in the gel and bulk phases. This results in the particle size depending not only on the temperature but also on the solvent chemical potential in the bulk. Ultrasmall-angle x-ray spectroscopy (USAXS) experiments are performed for an increasing concentration of the microgels above and below the volume phase transition. The Guinier region of scattering shows distinct de-swelling of the particles as the concentration is increased. Comparisons are made with particle sizes determined via dynamic light scattering (DLS).

Methods and Materials

The temperature-sensitive poly(*N*-isopropylacrylamide) microgel particles used in this study were synthesized via an emulsion polymerization method [1]. This method yields particles with a very narrow molecular weight distribution. The concentration of particles used for the USAXS experiments ranged from 1 to 5 wt%. Cells specifically designed for use in the USAXS temperature control setup (with an x-ray path length of 2 mm and polyimide windows) were used. All samples were equilibrated at the experimental temperature for 20 minutes before any measurement was taken. Scattering intensities were measured at 30° and 34°C. Deionized water was used as a blank for all samples.

Results

Figures 1 and 2 show the x-ray scattered intensity (I) versus the scattering vector (q) after the data had been processed to eliminate the effect of slit smearing. A plot of I versus q^2 at low q values, also called a Guinier plot, was used to estimate the particle size R_g , as tabulated in Table 1. The particle size in the extremely dilute concentration limit as measured from DLS is shown in Table 1 as well.

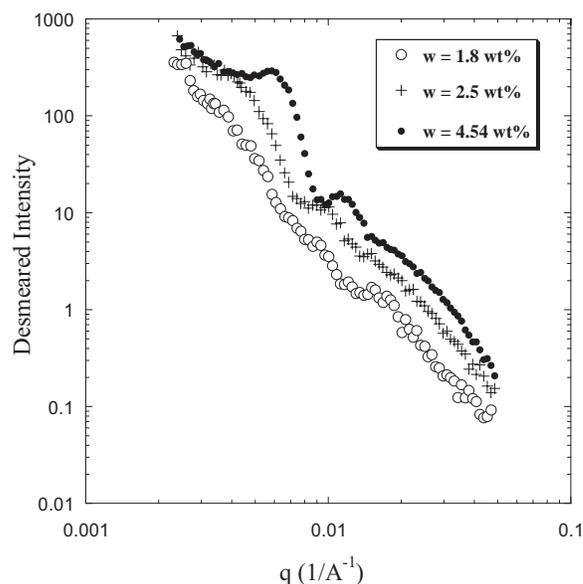


FIG. 1. Desmeared scattered intensity versus scattering vector as measured by USAXS for different microgel concentrations at 30°C.

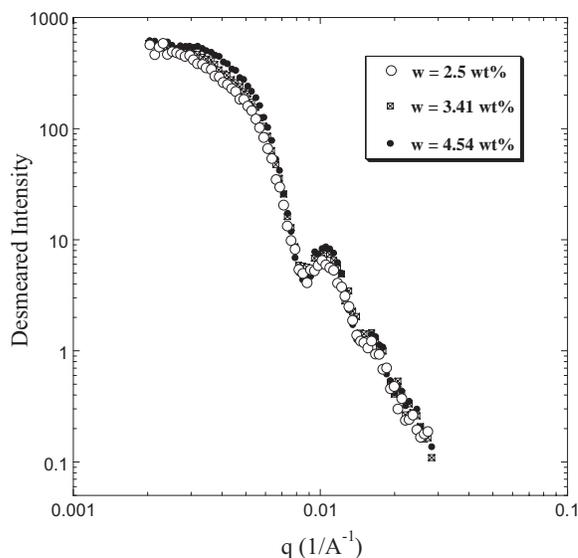


FIG. 2. Desmeared scattered intensity versus scattering vector as measured by USAXS for different microgel concentrations at 34°C.

TABLE 1. Comparison of sizes measured by using USAXS (high-concentration samples) and DLS (zero concentration limit) for different concentrations and temperatures.

Sample ID	Conc. (wt%)	Temp. (°C)	Rg (nm) Light Scattering	Rg (nm) USAXS, Guinier Plot
ANL B-01	2.5	30	136.4	44.3
ANL B-02	1.8	30	136.4	52
ANL B-stock	4.54	34	45.8	35
ANL B-07	3.4	34	45.8	38.5
ANL B-01	2.5	34	45.8	41.8

Discussion

These USAXS experiments revealed valuable information about the microstructure of the microgel particles. The particles were observed to undergo a distinct de-swelling as their concentrations were increased. The particle size determined from x-ray scattering at an elevated concentration was much smaller than the size measured from DLS experiments carried out with dilute suspensions.

This kind of de-swelling had been observed previously in bulk gels when they were placed in contact with a suspension of nonpenetrating polymer [2]. The polymer could penetrate the bulk gels, thus causing the osmotic pressure in the suspension to increase. This eventually led to a de-swelling of the gel phase. Such an analogy can be applied to this system of microgel particles where the increase in the concentration of the microgels in the suspension causes increases in the osmotic pressure of the suspension. This leads to a decrease in the chemical potential of the water in the bulk phase, thereby causing the de-swelling of the microgel particles.

Acknowledgments

The assistance of J. Ilavsky and P. Jemian with the USAXS measurements is greatly appreciated. UNICAT is supported by the University of Illinois at Urbana-Champaign, Materials Research Laboratory (U.S. Department of Energy [DOE]; State of Illinois Board of Higher Education, Higher Education Cooperation Act; and National Science Foundation); Oak Ridge National Laboratory (DOE under contract with UT-Battelle, LLC); National Institute of Standards and Technology (U.S. Department of Commerce); and UOP LLC. Use of the APS was supported by the DOE Office of Science, Office of Basic Energy Sciences, under Contract No. W-31-109-ENG-38.

References

- [1] H. Senff and W. Richtering, *J. Chem. Phys.***111**, 1705-1711 (1999).
- [2] H. Inomata, K. Nagahama, and S. Saito, *Macromolecules* **27**, 6459-6464 (1994).