Mater. Res. Soc. Symp. Proc. Vol. 840 © 2005 Materials Research Society Q7.11.1

USANS as a Probe of Large-Scale Structure in Attractive Colloidal Glasses of Block Copolymer Micelles

Mark A. Crichton, Neil S. Forbes, Surita R. Bhatia
Department of Chemical Engineering
University of Massachusetts Amherst
686 North Pleasant Street, Amherst, MA 01003 U.S.A.

ABSTRACT

We have used ultra-small-angle scattering (USANS) and fluorescence microscopy to show the existence of large-scale structure in attractive colloidal glasses composed of block polyelectrolyte micelles. Our systems display evidence of surface scattering, with the scattered intensity I at low scattering vector q scaling as $I \sim q^x$ with x in the range –3 to –4. We believe this is due to surface scattering from large, highly polydisperse aggregates with rough interfaces. USANS may provide an ideal way to distinguish fractal colloidal gels and colloidal glasses.

INTRODUCTION

Arrested or jammed states of soft matter, such as colloidal glasses and fractal colloidal gels, are interesting from both a fundamental point of view and in applications such as emulsions, foams, cosmetics, and foods. Colloidal gels and glasses can exhibit similar rheological properties and dynamics, making them difficult to distinguish experimentally [1]. However, there are key structural differences. In colloidal gels, attractive forces dominate, leading to an "open," percolated structure characterized by a fractal dimension. Colloidal glasses can form from either repulsive or attractive particles; however, repulsive forces are dominant and lead to slowing of the dynamics. The microstructure is much denser and more "crowded" than in a fractal colloidal gel, and the expectation is that no large-scale structure should be present in such systems. This behavior has been verified experimentally for colloidal glasses of repulsive particles, also referred to as "repulsive glasses." However, there is little data on the large-scale structure of glasses formed from attractive particles, referred to as "attractive glasses."

Recently, we performed ultra-small-angle neutron scattering (USANS) on aqueous solutions of poly(styrene)-poly(acrylic acid/ethyl acrylate) (PS-PAA/EA), which forms spherical micelles in water (Figure 1). Because of the hydrophobic EA groups, the micelles have an effective attraction that leads to formation of a viscoelastic solid or "gel"-like state at polymer concentrations above ~2 wt% [2,3]. We have shown previously that this viscoelastic solid state can be considered an attractive glass [2] where the strength of attraction is inversely related to the degree of hydrolysis of the PAA/EA block, f. In this study, we combine results from small-angle neutron scattering (SANS), USANS, and fluorescence microscopy to determine how the morphology of the jammed state changes with the strength of attraction.

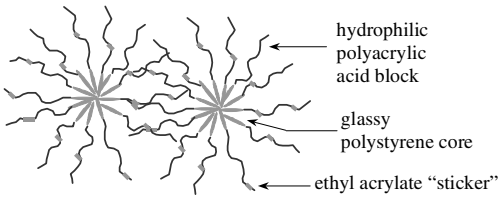


Figure 1. PS-PAA/EA micelles associated via ethyl acrylate (EA) stickers.

EXPERIMENTAL DETAILS

The diblock polymers was supplied by Rhodia Inc. as polystyrene-poly(ethyl acrylate). The molecular weight of the polystyrene-poly(ethyl acrylate) material was 2000 g/mol of polystyrene, and 19468 g/mol of poly(ethyl acrylate). The polymer was supplied as an aqueous suspension of latex particles of approximately 40 wt.%. The hydrolysis reaction was run with 10 wt.% polymer in water at 363 K. When the polymer solution reached 363 K, a 2M NaOH aqueous solution was added dropwise. The amount of NaOH added was dependent on the desired degree of hydrolysis. The reaction mixture was then held at 363 K for 24 h. The final degree of hydrolysis was determined using a 200 MHz ^{1}H NMR instrument. After hydrolysis, the polymer was dialyzed using regenerated cellulose membranes with a molecular weight cutoff of 6000-8000 (SpectraPor 1, Spectrum Laboratories) against an aqueous NaOH solution at pH 10 for about one week. This was done to remove impurities and normalize the charge density along the polymer backbone.

SANS data were recorded on the 30-meter small-angle instrument NG3 at the NIST Center for Neutron Research (NCNR), and USANS experiments were performed on NCNR's perfect crystal SANS instrument, BT5. Samples for USANS and SANS were prepared by dissolving freeze-dried polymer in D_2O (Cambridge Isotope Laboratories) and stirring for several days at 353 K. Spectra were obtained at 25°C for a polymer concentration of 4.0 wt.%. Quartz sample cells with a path length of 1 mm were used. The USANS and SANS data together cover a q-range of approximately 0.00005 Å^{-1} < q < 0.3 Å^{-1} (where $q = 4\pi/\lambda \sin 2\theta$ with θ = half the scattering angle and λ = wavelength of the incident neutrons).

Fluorescence microscopy was performed on samples with a polymer concentration of 2.0 wt%. The samples were prepared by dissolving freeze-dried polymer in nanopure water and stirring for several days at 353K. The samples were then allowed to cool to room temperature. To the samples, 6.1×10^{-7} of BODIPY® 505/515 (Molecular Probes) was added. The samples were then stirred to disperse the dye and stored in the dark at room temperature for 24 hours to allow the gel to equilibrate. After this, a small amount was placed between a glass slide and cover slip and placed into an Olympus IX71 microscope equipped with an EGFP filter set.

Confocal microscopy was performed as well. The sample preparation is similar to the fluorescence microscopy experiments. The dye used was 5-dodecanoyl-aminofluorescein (Molecular Probes), of which 0.01 mmol of dye was added to each sample. The samples were then mounted on a modified glass slide, which kept the sample thickness at about 100 microns. A Leica TCS SP2 confocal microscope was used to obtain photographs of the sample. An argon ion laser was used to excite the fluorophore at a wavelength of 514nm. Both the fluorescence and confocal micrographs were analyzed using the ImageJ software package.

RESULTS

Figure 2 shows the combined USANS and SANS spectra for a series of micellar gels with decreasing strength of attraction, from strongly attractive ($f = 0.44$) to weakly attractive ($f = 0.97$). A broad peak is observed in the SANS spectra, corresponding to intermicellar correlations. No peak is observed in the low q regime probed by USANS, as is sometimes present if large aggregates with a well-defined characteristic length scale are present. Rather, we obtain a power-law dependence over a large range of q, with the scattered intensity I at low q scaling as $I \sim q^x$. This indicates large-scale structure that persists over a range of length scales. That we observe this behavior down to $q = 0.00005$ Å^{-1} indicates that the largest aggregates are likely larger than 10 μm.

To analyze this data, we extend the classical expression for $I(q)$ to include the low q regime as follows:

$$I(q) = N(\Delta\rho_b)^2 P(q)S(q) + Aq^x \qquad (1)$$

where N is the number density of micelles, $\Delta\rho_b$ is the difference in scattering length density, $P(q)$ and $S(q)$ are the form and structure factor, respectively. Added to this is the term Aq^x, which is a simple power law to fit the USANS data. A and x are fitting parameters. For the form factor, $P(q)$, we used a polydisperse sphere model. This model contains two parameters, R, which we interpret as the radius of the micelle, and σ, the width of the size distribution. For the structure factor, an adhesive hard sphere (AHS) model was used to describe the interactions between micelles. The fitted parameters in this model are R_{HS}, the radius of interaction; τ, the stickiness parameter; and ϕ, the volume fraction. The details of how we applied these models are given elsewhere [4]. The inset in Figure 2 shows a sample data fit, and the parameters obtained from the fits are given in Table I.

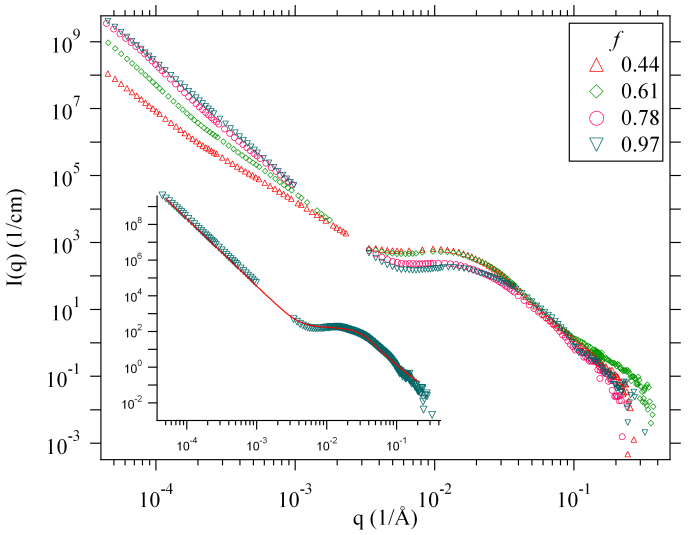


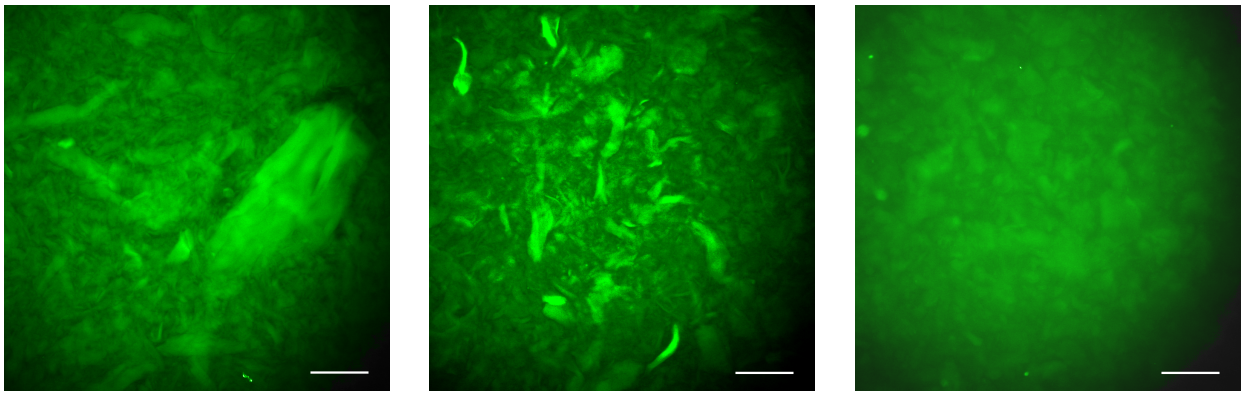
Figure 2. USANS and SANS spectra for attractive glasses of PS-PAA/EA micelles. Spectra are shown for a series with decreasing strength of attraction, from strongly attractive ($f = 0.44$) to weakly attractive ($f = 0.97$). The inset shows a sample fit to the combined SANS/USANS data.

Table I. Parameters from fits to the neutron scattering data.

f	R (Å)	R_{HS} (Å)	σ (Å)	x
0.44	114.6 ± 1.0	140.4 ± 0.3	28.8 ± 1.0	-2.90
0.61	108.1 ± 1.0	148.7 ± 14.9	27.7 ± 1.5	-3.11
0.78	94.7 ± 1.7	96.0 ± 32.1	25.0 ± 2.4	-3.55
0.97	79.4 ± 1.5	79.4 ± 26.3	21.0 ± 2.0	-3.76

We find low-q exponents, x, in the range –2.9 to –3.8. Moreover, as the strength of attraction decreases (f increases), the exponent x systematically decreases, approaching a value of –4. Exponent ranges between –3 and –4 are indicative of surface scattering, while exponents in the range of –1 to –3 are characteristic of mass fractals. The limit of –4 corresponds to smooth interfaces, while scattering from rough surfaces yields exponents closer to –3. Thus, we believe that we have large, compact, polydisperse aggregates with "rough" interfaces. The interfaces between these aggregates and the surrounds becomes smoother as the strength of attraction is decreased. This confirms earlier work that these systems are attractive glasses, rather than an associated network of micelles (i.e., a fractal gel). Similar low-q surface scattering has been observed in dense colloid-polymer gels with depletion attractions [5] and in attractive glasses of colloidal silica [6].

The fluorescence microscopy photos for f values of 0.44, 0.61 and 0.97 are shown in Figure 3. The bar in the micrographs represents 100 μm. In the images, the brighter regions represent where the BODIPY dye has concentrated. In our case, we assume that the hydrophobic polystyrene would be the most favorable for the dye to partition in. The images show that at low values of f, where the attraction between micelles is greatest, we see the formation of aggregates with length scales of 10-100 μm, confirming the USANS results. As f increases, we see that the number and size of these aggregates appears to diminish.



(a) (b) (c)

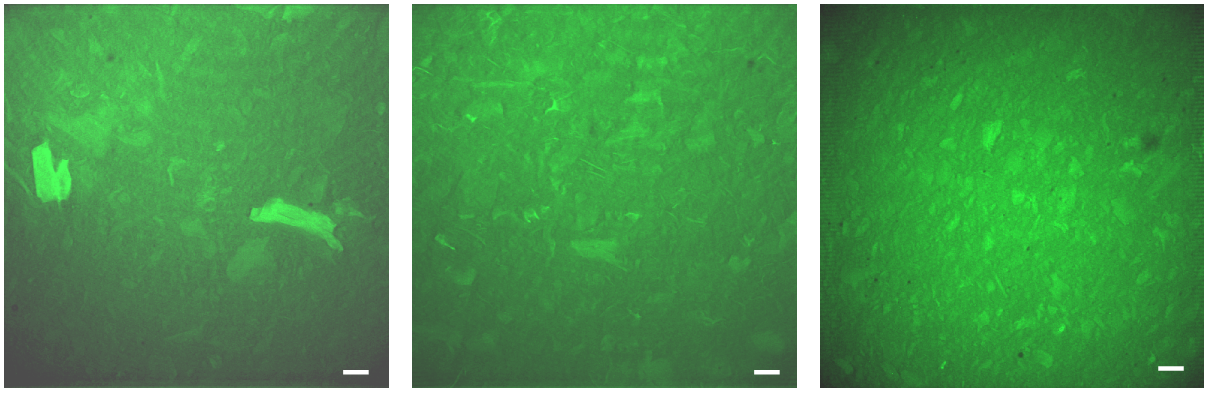
Figure 3. Fluorescence micrograph of 2wt% PS-PAA/EA gel in water for (a) f = 0.44, (b) f = 0.61, and (c) f = 0.97. Bar represents 100 μm.

In order to quantify this observation, image analysis was performed using several micrographs for each sample. Each photograph was segmented into bright and dark regions. After segmentation, the area of the aggregates was determined, and a distribution of aggregate areas was generated. Both of these steps were performed with ImageJ software. Table II summarizes the results. Note that the average aggregate sizes are in the range 20-40 μm. Moreover, the aggregates are highly polydisperse as indicated by the large width of the distribution. Again, these findings confirm our USANS results. The polydispersity in aggregate size seems to diminish as the strength of attraction decreases, as shown by the decreasing width of the distribution. Finally, both the images and analysis show the disappearance of extremely large aggregates (sizes > 100 μm) as the strength of attraction decreases.

Table II. Summary of results from image analysis on fluorescence microscopy images. Characteristic length is calculated as the square root of the area.

Fluorescence Micrographs				
f	Average Area (μm^2)	Width of Area Distribution (μm^2)	Average Length (μm)	Width of Distribution (μm)
0.44	1490.0	6694.0	38.6	81.8
0.61	441.2	1210.9	21.0	34.8
0.97	558.6	1576.7	23.6	39.7

For the confocal experiments, a similar analysis was used. The micrographs are shown in Figure 4, and the bar in the micrographs represents 100 μm. Image analysis was performed on several hundred images for each sample, and the results are given in Table III. The values for the average size are somewhat larger than from the fluorescence micrographs, in the range 35-50 μm, but the same trends are seen in the confocal images as in the fluorescence microscopy images.



(a) (b) (c)

Figure 4. Confocal micrograph of 2 wt% PS-PAA/EA gel in water for (a) $f = 0.44$, (b) $f = 0.61$, and (c) $f = 0.97$. Bar represents 100 μm.

Table III. Summary of results from image analysis on confocal microscopy images. Characteristic length is calculated as the square root of the area.

Confocal Micrographs				
f	Average Area (μm^2)	Width of Area Distribution (μm^2)	Average Length (μm)	Width of Distribution (μm)
0.44	2298.1	6074.5	47.9	77.9
0.61	2147.1	2868.1	46.3	53.6
0.97	1246.0	2248.6	35.3	47.4

CONCLUSIONS

USANS and microscopy shows the existence of large-scale structure in micellar gels of block polyelectrolytes. The low q scattering is not indicative of fractal aggregates; rather, surface scattering is observed from large, polydisperse, dense aggregates with rough interfaces. The interface seems to become smoother as the strength of attraction is decreased, and the low q exponent tends towards -4. Together with the results of Shah et al. [5] and Pontoni and Narayanan [6], our results suggest that ultra-small-angle scattering may be an excellent method to distinguish between attractive colloidal gels, attractive colloidal glasses, and repulsive colloidal glasses.

ACKNOWLEDGMENTS

USANS and SANS data were taken with the assistance of John Barker, Steve Kline, Boualem Hammouda, and Derek Ho at NIST. This portion of the work utilized facilities supported in part by the National Science Foundation (NSF) under Agreement No. DMR-0086210. We acknowledge the support of the National Institute of Standards and Technology, U.S. Department of Commerce, in providing the neutron research facilities used in this portion of the work. The confocal microscopy images utilized the central facilities of the NSF-sponsored UMass MRSEC on Polymers under DMR-0213695. Partial support for M.A.C. was provided by the NSF under grant CTS-0238873.

REFERENCES

1. H. Tanaka, J. Meunier, and D. Bonn, Physical Review E **69**, 031404 (2004).
2. S R Bhatia and A Mourchid, Langmuir **18**, 6469-6472 (2002).
3. S. R. Bhatia, A. Mourchid, and M. Joanicot, Current Opinion in Colloid and Interface Science **6**, 471-478 (2001).
4. M. A. Crichton and S. R. Bhatia, Journal of Applied Polymer Science **93**, 490-497 (2004).
5. S. A. Shah, Y. L. Chen, S. Ramakrishnan, K. S. Schweizer, and C. F. Zukoski, J Phys: Conden Matter **15**, 4751-4778 (2003).
6. D. Pontoni and T. Narayanan, J Appl Cryst **36**, 787-790 (2003).