Characterization of Ultra-High Molar Mass Polyacrylate Emulsions by Asymmetrical Flow Field-Flow Fractionation Coupled to Multi-Angle Light Scattering

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Introduction

Acrylic polymer emulsions and other water-based acrylic polymer products are important materials for the graphic arts and industrial coating industries, and are commonly the main ingredient in latex paints. As these samples often contain ultra-high molar mass polymers, they are challenging to separate and accurately characterize by chromatographic methods such as Size Exclusion Chromatgraphy (SEC). An alternative technique is Asymmetrical Flow Field-Flow Fractionation (AF4), which uses an open channel architecture for size separation instead of a packed column, avoiding the loss of large emulsion materials on the column packing material. [1,2] Thus the separation range of Field-Flow Fractionation (FFF) is larger than the one of SEC (see Figure 1).

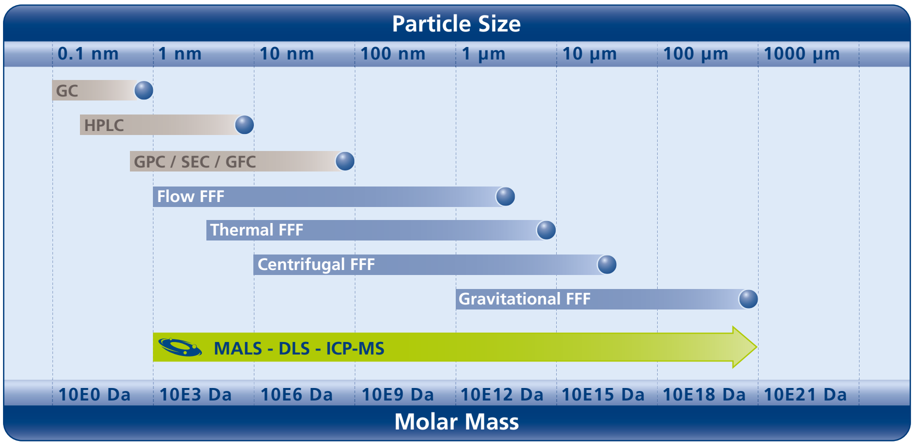

Figure 1: Separation Range for SEC and FFF technologies.

Figure 2 illustrates the principle of AF4: in the open channel a combination of cross flow and channel flow causes size separation over the course of analysis, with smaller molecules eluting before larger molecules.
In this work, AF4 coupled on-line to Refractive Index (RI) and Multi-Angle Light Scattering (MALS) detection was used to measure the molar mass and radius of three polyacrylate samples. Plotting these measurands against each other on a logarithmic scale provides information about polymer branching (conformation plot).

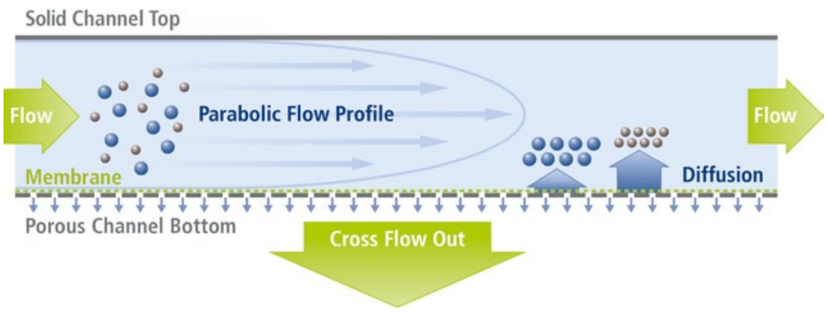

Figure 2: Schematic of the AF4 separation principle.

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Experimental Details and Results

Three aqueous acrylate emulsion samples of varying size, molar mass, and degree of branching were analyzed by AF4-RI-MALS. A 50 µL aliquot was diluted in 10 mL of nanopure water and rotated overnight to disperse. An injection volume of 20 µL was separated by AF4 with a detector flow of 0.5 mL/min.

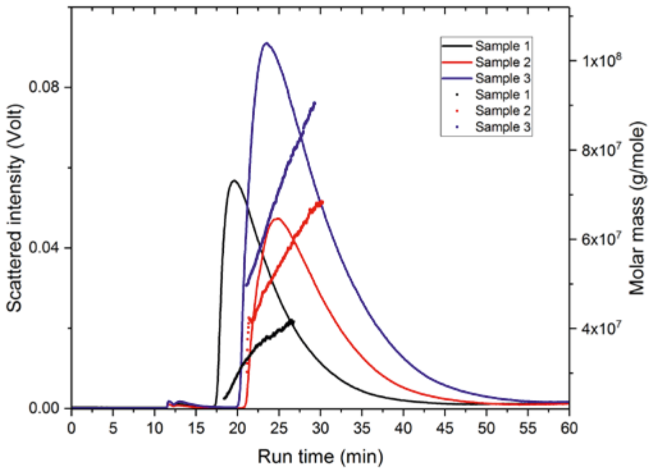

Figure 3: Molar mass of the three emulsion samples measured by AF4-RI-MALS.

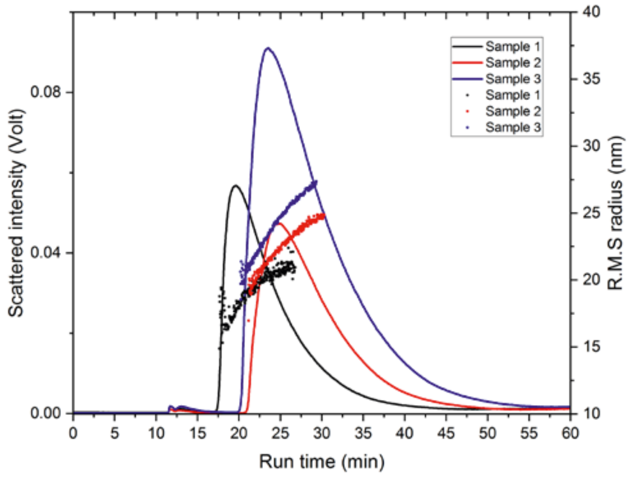

Figure 4: R.M.S. radius for the three emulsion samples measured by AF4-MALS.

Figure 3 shows replicate fractograms for the 90° MALS signal vs time, and molar mass measurements for each sample. The molar masses range from ~25 MDa to ~90 MDa illustrating the wide range separable by AF4, and also AF4's ability to separate molar mass species, which will likely be lost on an SEC column's packing material. Sample 1 elutes first and has the smallest molar mass; samples 2 and 3 elute at approximately the same time, however MALS-analysis reveals that sample 3 obviously contains a component of much larger molar mass.

Figure 4 shows replicate fractograms for the 90° MALS signal vs time, and radius measurements for each sample. Sample 1 is the smallest sample in size; samples 2 and 3 are similar in size with sample 3 containing a component of slightly larger measured radius. The radius for the three samples range from ~16 nm to ~27 nm, or about 32 nm to 54 nm in diameter.

Plotting the log R vs the log M results in a conformation plot, shown in Figure 5. This provides a means to compare changes in size with changes in molar mass; a shallower slope on this graph indicates that a polymer's molar mass is increasing with relatively little increase in size, and is likely to be more highly compact or branched. A slope of 0.5 - 0.6 is common for polymers with a random coil geometry, and sample 1's conformation plot slope of 0.54 indicates this. Sample 2 and 3's slopes of 0.45 and 0.44, respectively, indicate that they are more compact and likely more branched than sample 1.

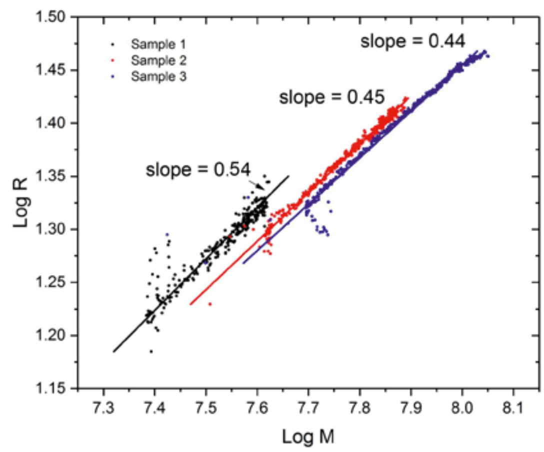

Figure 5: Conformation plot for the three acrylate emulsion samples.

Conclusion

AF4-RI-MALS was used to separate and characterize three polyacrylate emulsions by radius, molar mass, and degree of branching. Even for samples with radii up to ~30 nm and MW up to ~100 MDa, AF4 provides robust separation, making it an ideal technique for analysis of such large macromolecules.

References

[1] Makan A.C., Williams R.P., Pasch H., Macromolecular Chemistry and Physiscs, 2016, 217(18), 2027-2040.
[2] Makan A.C., Spallek M.J., du Toit M., Klein T., Pasch H., Journal of Chromatography A, 2016, 1442, 94-106.