Investigation of Polyacrylates Molecular Weight and Structure Using Thermal Field-Flow Fractionation Coupled to Multi Angle Light Scattering

General Information

ID0065

Application	Polymer
Technology	TF3-MALS-RI
Info	Postnova TF2000 Thermal FFF, PN3621 MALS, PN3150 RI
Keywords	Thermal Field-Flow Fractionation, Multi Angle Light Scattering, Polymer, Polyacrylates, Acrylic Acid, Cross-linking

Introduction

Acrylic polymers (polyacrylates) are widely used in many industrial and consumer applications, such as paints and coatings. The polymers are often complex combinations of monomer units [1] and the extent of cross-linking or branching determines the polymer's physical properties and therefore determines which application(s) a given formulation will be most applicable for. In this application note, we demonstrate the use of thermal field-flow fractionation (TF3) for the characterization of acrylic polymers.

In TF3 a separation field is established by applying a temperature gradient perpendicular to the channel. The top channel wall is heated and the bottom wall is cooled, driving polymers towards the cold wall by thermal diffusion. Smaller polymers can diffuse into the faster flow profiles of the laminar channel flow and elute to detectors sooner than larger polymers [2]. A schematic for the TF3 channel is shown in Figure 1.

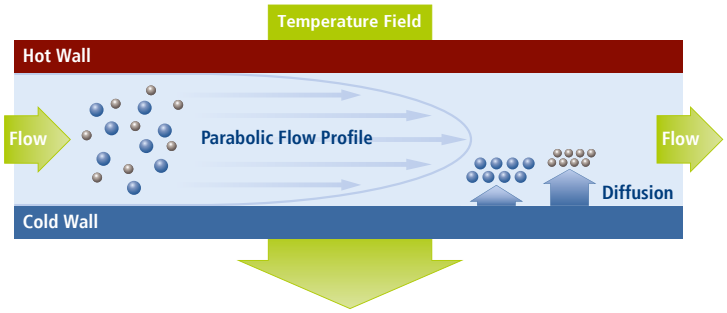

Figure 1: Schematic of the TF3 channel.

The characterization of three different acrylic polymer formulations was performed by coupling TF3 to multi angle light scattering and refractive index detectors (TF3-MALS-RI) enabling access to their molecular weight distributions as well as their radii of gyration. In addition, plotting the log of molecular weight (log M) versus the log of radius of gyration (log R_g) yields a conformation plot, which can be used to estimate the degree of polymer cross-linking.

Experimental Details and Results

To separate and characterize the polymers, a TF3 system (Postnova TF2000) was used with two detectors monitoring the eluent. Firstly, a Postnova 21-angle multi-angle light scattering detector (MALS, PN3621) for measuring the radius of gyration (R_g); and secondly a refractive index detector (RI, PN3150) which is sensitive to polymer concentration, and in combination with MALS can provide molecular weight measurements. A carrier solution of tetrahydrofuran (THF) was used.

Figure 2 shows fractograms with the MALS signal as solid lines, and the molecular weight calculated from the MALS and refractive index signal. However, even though the elution order of the three different samples does not seem to follow a simple trend with molecular weight (probably due to different level of impurities in the samples [3,4], we do observe good separation of each sample as demonstrated by the consistently increasing molecular weight profiles shown by the dots across each peak. The average molecular weights for the three samples were found to vary widely: 13 MDa, 56 MDa, and 93 MDa.

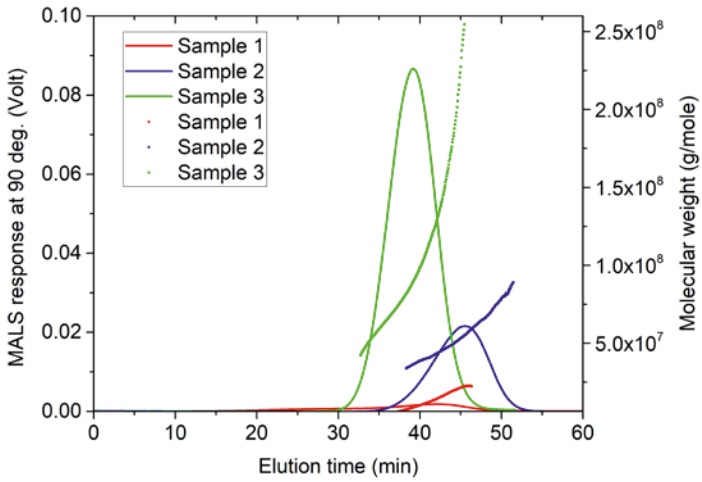

Figure 2: Fractogram for three acrylate samples separated by TF3. The curves correspond to MALS response at 90°; the dots are the measured molecular weight at each time point.

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Figure 3 shows the same MALS signal with the radius of gyration plotted across the fractograms. A significant population of the polymer sizes observed are above 75 nm in radius, which would likely not be well separated by size exclusion chromatography, but are easily separated by TF3. The average radii of gyration for the samples did not follow the same trend as MW, with measured sizes of 111 nm, 91 nm, and 68 nm, respectively.

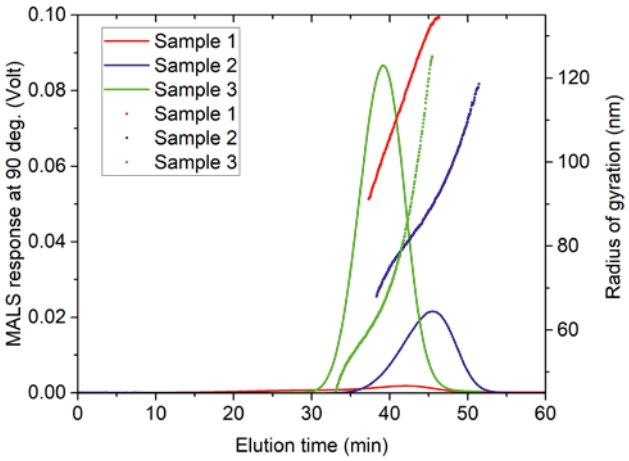

Figure 3: Fractogram for three polyacrylate samples separated by TF3. The curves correspond to MALS response at 90°; the dots are the measured radius of gyration at each time point.

In Figure 4 we have plotted the log of R_g vs the log of MW. A slope of 0.33 suggests that the molecule is highly cross-linked and spherical in shape. A molecule with random coil geometry will have a slope around 0.5 to 0.6, and a steeper slope, such as a value of 1 or more, indicates rod-like geometry. This makes sense conceptually: if a molecule is adding mass but not increasing in radius as quickly, it must be growing in all three dimensions and taking on a spherical shape. Here we see that sample 1 is spherical in shape and likely to be highly branched or crosslinked, while samples 2 and 3 are less crosslinked and likely have a random coil geometry. This information is very important to know as it affects physical properties of the polymer and therefore the appropriate application.

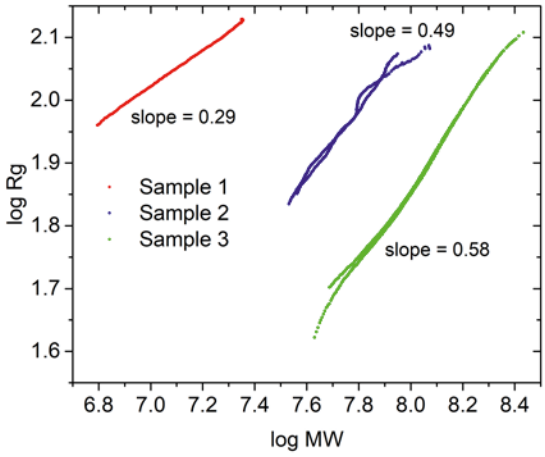

Figure 4: Conformation plot, with log MW plotted against log R_g

Conclusion

From the data presented here, we see that TF3-MALS-RI can separate large polymer molecules and provide molecular weight and Rg values. Most chromatography columns would filter out some or all polymer molecules this large, resulting in incorrect determination of their size and molecular weight distributions. These data also demonstrate how TF3-MALS can be used to elucidate the polymer structure, which can provide insight into why different formulations have different physical properties.

References

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