AN1002: Characterizing the Average Composition and Molar Mass Distributions of a Copolymer by SEC-MALS-dRI-UV

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Summary

The chemical composition of a copolymer material has a substantial impact on its properties and performance. Defining a composition profile is therefore an essential aspect of copolymer product development. Since copolymer composition often varies considerably with molecular weight (MW), a detailed analysis is required in copolymer R&D.

Traditional polymer characterization techniques such as size exclusion chromatography coupled with differential refractive index detection (SEC-dRI) or nuclear magnetic resonance (NMR) are either insufficient to perform a comprehensive analysis, or involve significant labor, complexity and/or cost.

This application note demonstrates how both the absolute molecular weight *and* composition of random-copolymer samples with a UV-absorbing component may be determined quickly and accurately, without a fraction collection step or NMR analysis. The technique utilizes size exclusion chromatography combined with analysis by three on-line detectors: multi-angle light scattering, differential refractive index and UV/Vis absorbance (SEC-UV-MALS-dRI). Weight fractions of poly(styrene-co-acrylic acid) (PSAA) samples were analyzed using the triple-detector system and ASTRA® software for macromolecular characterization. Results were found to be in good agreement with the reference values determined by ^{1}H NMR spectroscopy.

Some common forms of polystyrene acrylic.

Introduction

From controlled release agents in novel pharmaceuticals to materials for advanced carbon capture technology, newly-developed industrial copolymers incorporate advanced functionality and performance. The need for greater insight and understanding into polymer composition has stimulated significant advances in routine polymer characterization technology.

Gel permeation chromatography (GPC) with differential refractive index (dRI) detection is the most common approach to determining the MW and MW distribution of typical polymers. However, GPC-dRI cannot distinguish chemical composition and usually cannot be calibrated correctly for copolymers.

Size exclusion chromatography coupled with multi-angle static-light scattering (SEC-MALS) and differential refractive index (dRI) detection is widely considered the technique of choice to deliver accurate and robust measurements of polymer molecular weight (MW) and MW distri-

bution. Where conventional single detector SEC only delivers a comparative MW result based on reference material, SEC-MALS generates an absolute measurement of MW without the need for potentially inappropriate external calibration. However, MALS and dRI alone are not sufficient to provide comprehensive compositional analysis of copolymers.

A common characterization technique for copolymer analysis is proton nuclear magnetic resonance (^{1}H NMR) which excels at determining chemical identity. Standard NMR is only able to provide measurements of the sample-average composition. ^{1}H NMR can be used with preparative fractionation to obtain a coarse size/composition distribution, but this may be impractical to perform regularly. On-line GPC-NMR, GPC-FTIR and 2D-LC instruments have been developed to provide the average chemical composition at elution moment and molecular weight; however, these instruments are usually associated with high capital and operational cost. A technique similar to SEC-MALS, combining the continuous measurement aspect of SEC with an accurate chemical and molecular weight analysis, would be highly beneficial to certain copolymer development.

Depending on the polymerization mechanism and process, the chemical composition of a copolymer material can vary greatly across the molecular weight distribution of the polymer. When composition varies with size, the copolymer's specific refractive index increment *dn/dc* – used in both concentration and light scattering analyses – will change with elution volume during an SEC separation. Therefore, accurate molar mass data cannot be obtained for specific size fractions with SEC-MALS alone.

The addition of a third detection unit offers a solution to this issue. As many monomers include chromophore absorbing species, UV detectors are widely employed to enhance the analytical productivity of SEC-MALS for compositional studies. Modern UV, MALS and dRI detection units are compatible with a range of separation techniques including GPC, HPLC and field-flow fractionation. Comprehensive copolymer characterization can be attained using a variety of separation platforms.
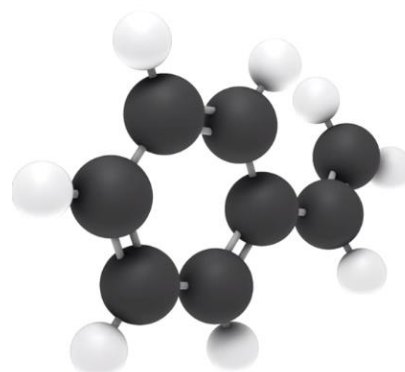

Figure 1: Basic structure of a styrene monomer

To demonstrate the utility of a three-detector SEC system for measuring both composition and molar mass distribution, three poly(styrene-co-acrylic acid) (PSAA) standards underwent compositional analysis with a SEC-MALS-dRI-UV system illustrated in Figure 2. The results were then validated against those provided by the manufacturer using NMR spectroscopy.

Figure 2. Wyatt's DAWN detector and Optilab dRI detector provide absolute polymer characterization in conjunction with size-based separation techniques.

Materials and Methods

Three samples of PSSA were purchased from Polymer Source, Inc. Following separation, the fractionated polymers were characterized using a three-detector setup consisting of MALS (DAWN®), dRI (Optilab®) and UV detection at 254 nm (ABI 785A).

System Validation

The UV-MALS-dRI system was validated with a 30 kDa polystyrene (PS) reference standard. Figure 3 shows the MW distribution for the sample. The UV extinction coefficient was calculated using ASTRA® macromolecular characterization software.
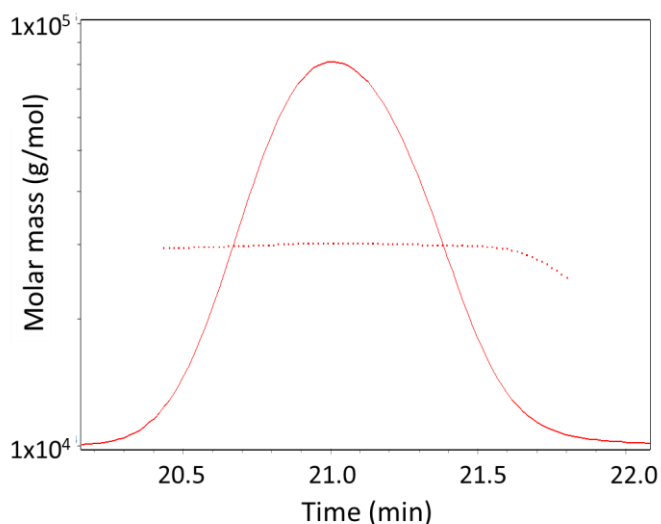
Results and Discussion

Figure 4 shows the reaction scheme for PSAA, including the reactive monomers ethenylbenzene (styrene) and t-butyl acrylate and intermediary product poly(styrene–butylacrylate). The final product poly(styrene-co-acrylic acid) was obtained by hydrolysis of the intermediary product. The UV-absorbing component of the final PSAA product is polystyrene (PS). The molecular weight and polydispersity index (PDI) were calculated from the intermediary product poly(styrene-co-t-butyl acrylate).

Copolymer MW and composition were then calculated using the "*Protein Conjugate*" template in ASTRA (despite the name, this template may be applied to copolymer

analysis). The calculation requires *dn/dc* values and extinction coefficients for each homopolymer.

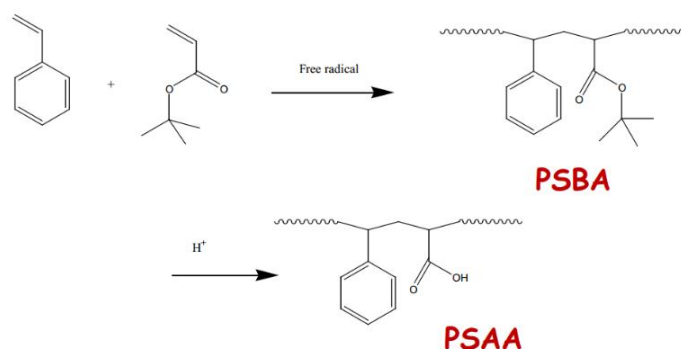

Figure 4. Reaction scheme for poly(styrene-coacrylic acid) (PSAA) from styrene and butyl acrylate.

MW and PS% vs. Elution Time

Figure 5 visualizes these data in the form of plots showing MW and PS% against elution time. The weight fraction percentage of PS was found to increase with elution time. This indicates there is a much greater concentration of the styrene monomer in the lower molecular weight region of the copolymer.
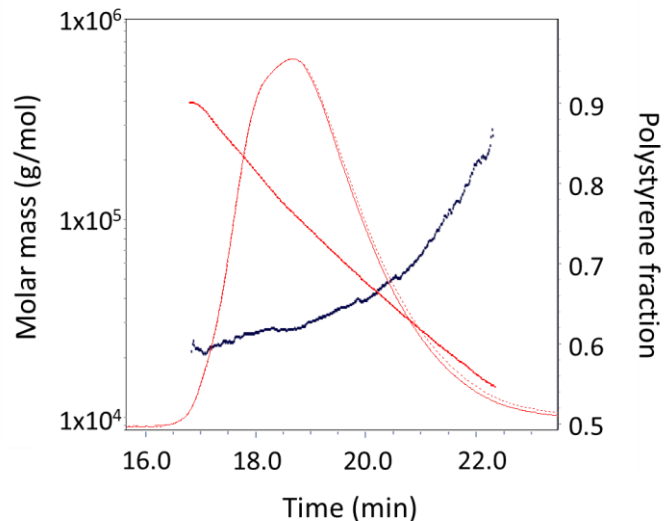

Figure 5. Plots of MW (red bold trace, left axis) and %PS (blue trace, right Y-axis) vs. elution time. PS weight fraction increases with elution time and hence with decreasing copolymer size. Thin dashed red plot is LS signal, thin red plot is RI chromatography.

Comparison with alternative methods

Table 1 summarizes results for the three PSAA samples generated with three-detector SEC-MALS and compares them with results from alternative techniques, GPC and 1H NMR. The results calculated by ASTRA are in good

agreement with those measured by 1H NMR spectros-copy.

	UV-MALS-RI			Other Methods	
Sample	M_n (kDa)	M_w (kDa)	PS%	M_w (kDa) by GPC	PS% by ^{1}H NMR
1	23.5	23.9	94.9	22	91
2	38	55	63.3	53	64
3	61	111	64.5	122	71

Table 1. Results from three-detector analysis are in good agreement with those measured by 1H NMR.

Conclusions

A triple-detector system comprised of MALS, UV and dRI detectors downstream of SEC, combined with ASTRA software, delivers absolute MW and provides information on the composition of random copolymers with a UV-absorbing component, without increasing the analysis time.

Moreover, since this method characterizes each small volume as it elutes from the SEC column, a full and contiguous composition distribution can be obtained.

Increased understanding of composition helps developers control the behavior of their copolymers and develop new materials that meet advanced product and commercial targets.