Characterizing composition and molar mass distribution of poly(styrene-co-acrylic acid) by MALS-dRI-UV detection following size exclusion chromatography

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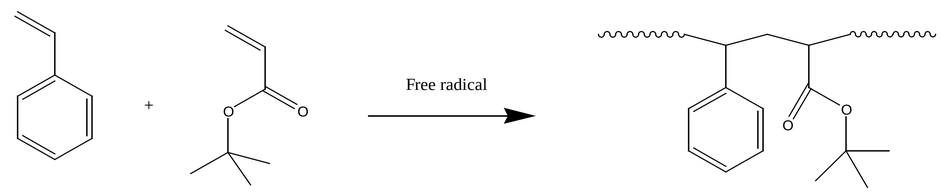
Abstract

Size exclusion chromatography (SEC) with multi-angle light scattering (MALS) has become the method of choice for characterizing molar mass distribution of polymers. These polymers are either homopolymers or copolymers. Characterizing copolymers is more challenging because of their heterogeneity in composition. Depending on polymerization mechanism and process, chemical composition of copolymers could vary among molar mass. As a result, not only molar mass but also polymer composition could change with elution volume during an SEC separation. When composition varies, the specific refractive index increment, *dn/dc*, will also vary. Since the composition is a parameter to be determined, accurate molar mass cannot be obtained by the traditional SEC-MALS method using a single *dn/dc* value. In this poster, we use poly(styrene-co-acrylic acid) standards to demonstrate the use of a three-detector system (MALS, dRI, and UV) for measuring both the composition and molar mass distribution. The results will be compared to the ones provided by the manufacturer using NMR spectroscopy.

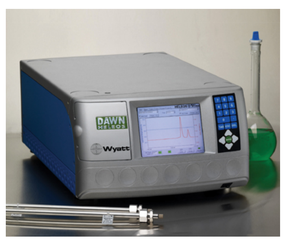
Sample Information



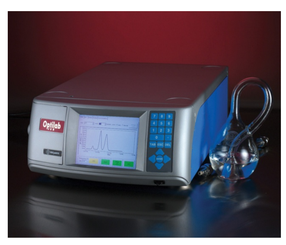
PSAA was purchased from Polymer Source, Inc. PS% was measured by ^{1}H NMR; molecular weight based on conventional SEC using PS standards for column calibration.

Instrument Setup

HPLC:	**Shimadzu**
MALS detector:	**DAWN HELEOS from Wyatt**
RI detector:	**Optilab rEX from Wyatt**
UV at 254nm:	**UV from ABI**



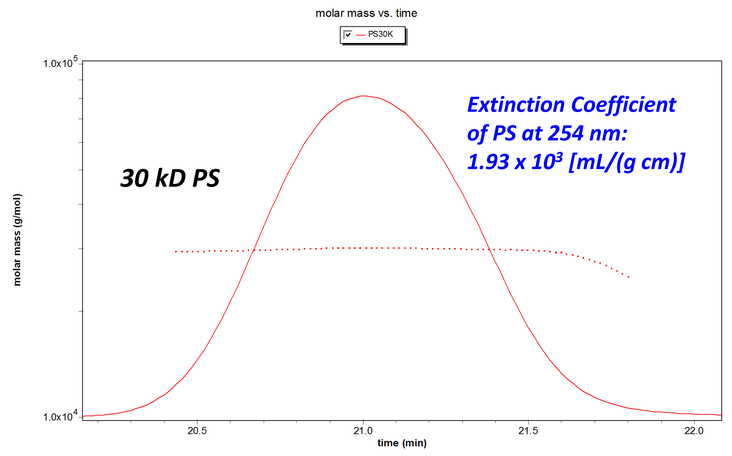
DAWN HELEOS



Optilab rEX

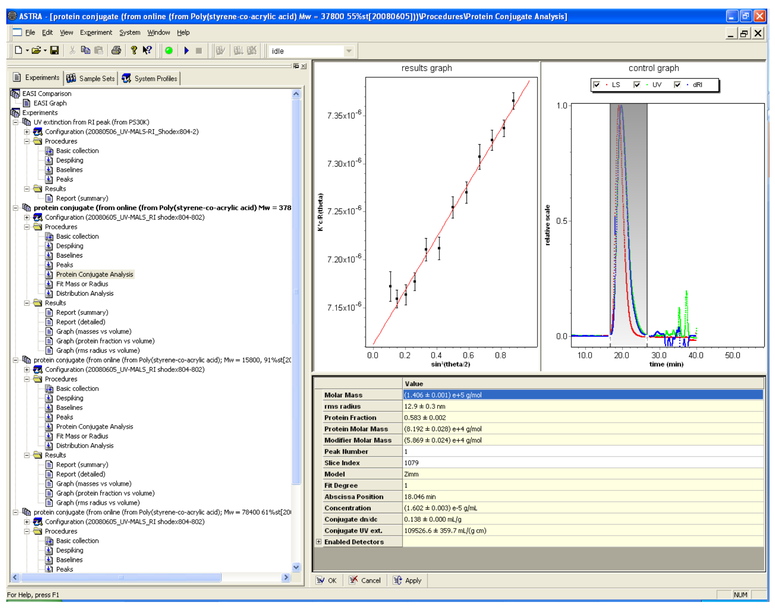
ABI 785A UV Detector

System Validation



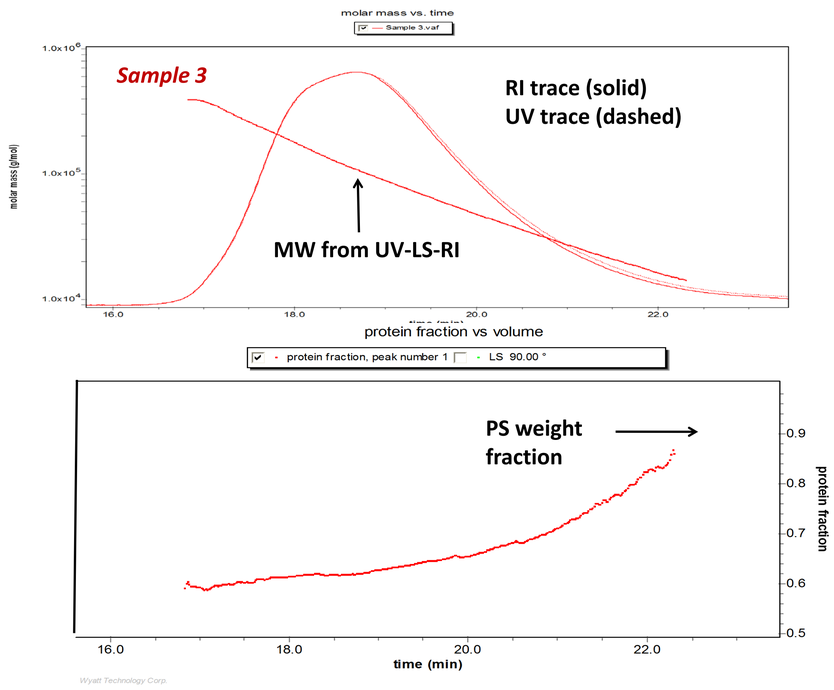
30 kD PS analyzed by UV-MALS-RI. UV extinction coefficient of PS was calculated using "UV extinction from RI peak" template in ASTRA V.

Composition Analysis by UV-MALS-RI



By entering dn/dc values and extinction coefficients for each homopolymer, both copolymer MW and composition can be calculated using "Protein Conjugate" template in ASTRA V.

MW and PS% *vs.* Elution Time



PS weight fraction (right Y-axis of bottom graph) was found to increase with elution time.

Comparison of results

	MALS			From other methods	
Sample	Mn (kD)	Mw (kD)	PS%	Mw (kD) GPC	PS% ^{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

Conclusions

- By adding UV-LS-RI detection to SEC, we can not only determine absolute MW but also composition for these random copolymers without increasing the analysis time.
- The weight fractions of poly(styrene-co-acrylic acid) samples determined by UV-LS-RI detection using ASTRA V are in good agreement with the ones measured by ^{1}H NMR spectroscopy.
- Since this method characterizes fractionated polymers by SEC, the composition distribution can also be obtained; whereas ^{1}H NMR can only measure the average composition.