

Molecular weight and the Mark-Houwink relation for ultra-high molecular weight charged polyacrylamide determined using automatic batch mode multi-angle light scattering

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ABSTRACT: This study presents an automatic batch mode (i.e., off-line) multi-angle light scattering (MALS) method for the molecular weight (MW) determination of ultra-high MW (UHMW) polyacrylamide (PAM) homopolymer and acrylamide copolymers. This method combines a MALS detector with a sample dilution and injection device that automatically delivers a concentration gradient from a stock solution. The automation makes it practical to use the batch MALS method for routine MW analysis of UHMW polymers. The automatic batch MALS analyses of a series of poly(sodium acrylate-co-acrylamide) (30:70 mol %) in 1.0M NaCl show a non-linear Mark-Houwink relation in the MW range of 1.2×10^6 to 12.6×10^6 g mol⁻¹. The entire molecular weight range can be fit with a quadratic relation or two linear equations, one for molecular weight up to 5.3×10^6 g mol⁻¹ and the other from 5.3×10^6 to 12.6×10^6 g mol⁻¹. The non-linear Mark-Houwink relation suggests that the extrapolation of the Mark-Houwink equation beyond the measured MW range into the UHMW regions can significantly overestimate the MW of the UHMW polymers. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43748.

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INTRODUCTION

Polyacrylamides (PAMs) refer to a broad family of water-soluble polymers made from acrylamide and other co-monomers. Ultra-high MW polyacrylamides (UHMW PAMs) ($>5 \times 10^6$ g mol⁻¹) are widely used as dewatering aids, flocculants, and viscosity modifiers in various industries such as water treatment, paper making, mining, and energy services.¹ Molecular weight is one of the most important properties influencing polymer performance in such applications. Because of the UHMW and potential for ionic character (i.e., charge), the MW characterization of UHMW PAMs is very challenging. Size exclusion chromatography (SEC) fails to provide an accurate MW because of polymer shear degradation and adsorption to column matrices.² In recent years, asymmetrical Flow Field Flow Fractionation has shown promise in characterizing UHMW biopolymers and particles.³ However, applications to UHMW PAMs are still very limited.⁴⁻⁶ Light scattering has long been used for MW characterization of PAMs. For several decades, academic and industrial researchers have used light scattering to study the solution behavior and viscosity-molecular weight relationships of PAM and its derivatives.⁷⁻¹⁹ There are, however, very few published studies on the light scattering analysis of these polymers in the UHMW regions.²⁰⁻²² Currently,

the MW of UHMW PAM is often estimated using intrinsic viscosity data and the Mark-Houwink equation. Owing to the lack of existing MW data in the UHMW region, the Mark-Houwink constants are often established with lower MW PAMs and thus need to be validated when used to determine the MW of UHMW PAMs.

The first objective of this article is to present an automatic batch mode multi-angle light scattering (MALS) method for reliable MW determination of UHMW PAMs, specifically poly(sodium acrylate-co-acrylamide) (30:70 mol %), abbreviated as 30 mol % anionic polyacrylamide or 30 mol % APAM, a widely used PAM product in various industrial applications. The automatic batch MALS method previously developed in our laboratory for the analysis of UHMW dextran, a branched polysaccharide, has been described elsewhere.²³ In an adaptation of this method, a MALS detector is connected to an automatic sample dilution and injection device to automatically deliver a concentration gradient. The automation improves sample throughput and makes it practical to use batch MALS for routine analysis of UHMW polymers. Relative to dextran, linear PAMs are much more viscous at the same MW, especially if charged, and, therefore, pose unique challenges to the batch MALS measurements. In this article, the sample preparation

and clarification procedures were optimized for UHMW 30 mol % APAM and an analysis of the data generated using the technique is presented.

The second objective of the present work is to establish Mark-Houwink parameters for 30 mol % APAM, covering the high to UHMW range. An accurate Mark-Houwink relation enables reliable estimation of MW based on intrinsic viscosity data. The automatic batch MALS method described herein was used to determine the MW of a series of 30 mol % APAM polymers with MW ranging from 1.2×10^6 to 12.6×10^6 g mol⁻¹. A non-linear Mark-Houwink relation was observed. Possible explanations and the significance of this observation are discussed.

EXPERIMENTAL

Synthesis of 30 mol % APAM

A series of 30 mol % linear APAM samples were synthesized via adiabatic solution polymerization of acrylamide and sodium acrylate in water using redox initiators and established methods.²⁴ After completion of the polymerization, a solidified wet gel product was obtained. The wet gel was granulated, dried, and ground into a fine powder which contained approximately 10% moisture. The moisture content in the polymer powder was measured using a moisture balance operated at 140 °C for 1 h. This information was subsequently used to correct the polymer concentration of the stock solutions for the batch MALS measurements.

Batch MALS Measurements

Polymer solutions were prepared in Milli-Q[®] high purity water at 0.25 wt % concentration of polymer actives and mixed with a cage stirrer (Jiffy Mixer, McMaster Part #3471K5) at 800 rpm at room temperature for 1 h to obtain dissolution. One sample (#9) was also dissolved with a stir bar at 200 rpm for 15 h.

The 0.25 wt % polymer solutions were further diluted with an aqueous mobile phase (1.0M NaCl) to a concentration of 0.005% (0.05 mg mL⁻¹ or 50 ppm) and stirred with a stir bar at 200 rpm for 15 h. The diluted solutions were then filtered through 1.2 μm syringe filters (Pall Life Science Acrodisc[®] 25 mm, PN 4488T) to remove dust and any other large particle contaminants. The filtered 50 ppm stock solutions were diluted sequentially to ten different concentrations with an automatic dilution and injection device, Calypso II, purchased from Wyatt Technology (Santa Barbara, CA), and then directly injected into a MALS detector, a Dawn HELEOS II purchased from Wyatt Technology. The Calypso II and MALS instruments have no temperature control. The solutions for batch MALS were kept at room temperature, approximately 23 ± 2 °C. The MALS cell temperature is slightly higher than room temperature at about 28 ± 2 °C. The Calypso II flow rate was set to 1.0 mL min⁻¹. The scattering data were collected at 17 different angles with an incident laser wavelength of 664 nm. Calibration of the MALS detectors was done using HPLC grade toluene. The data analysis was conducted with Astra 6 software provided by Wyatt Technology.

Intrinsic Viscosity Measurement

The intrinsic viscosity (IV) of the polymers was measured in 1.0M NaCl at 30 ± 0.02 °C using a Cannon Ubbelohde semi-micro dilution viscometer, size 75. The intrinsic viscosity values

were extrapolated from the linear plots of reduced specific viscosity versus concentration.²⁵ The units associated with IVs reported in this article are dL g⁻¹. The inherent error in the measurement of IV using the described technique is estimated to be 2 dL g⁻¹ or less.

Determination of Refractive Index Increment, dn/dc

SEC/MALS experiments were conducted in 1.0M NaCl at 30 ± 0.01 °C to determine the specific refractive index increment (dn/dc) by assuming 100% mass recovery. A Shodex OHpak SB-806M HQ column was used for the analysis. The flow rate was set at 1.0 mL min⁻¹. The Wyatt Optilab T-rEx Differential Refractometer was calibrated with a series of NaCl solutions of known concentration.

RESULTS AND DISCUSSION

Light scattering measurements can be performed in either “online” or “offline” mode. SEC/MALS is the most common online MALS technique and widely used in the MW determination of high MW polymers. One limitation of this technique is that on-column shear degradation typically occurs for UHMW polymers.² Batch mode MALS, that is, off-line MALS, does not use columns but rather directly measures the scattered light of dilute polymer solutions. The absence of columns allows for more accurate MW determination of UHMW polymers.²³ However, the UHMW and resultant high solution viscosity of these polymers pose challenges to the batch MALS analysis of the UHMW PAMs. Specific challenges in the present experiments, including dissolution of the polymer powder, clarification of the solutions, and interpretation of the data are addressed in subsequent sections.

Preparation of Polymer Solutions for Light Scattering Measurements

For UHMW 30 mol % APAM, one challenge in accurately making the light scattering measurement involves completely dissolving the powder polymers without causing shear-induced degradation of the polymer chains, thus causing inaccurately low molecular weight to be measured. A procedure has been developed in our laboratory to accomplish this: the powder polymers were prepared in Milli-Q[®] water at 0.25 wt % concentration and stirred with a cage stirrer at 800 rpm for 1 h. To validate that this method does not cause polymer molecular weight degradation, one sample (#9) was also dissolved with a very low shear technique employing a magnetic stir bar allowed to rotate at 200 rpm for 15 h. Table I shows the weight average MW determined for this sample as a function of the two different sample preparation methods. A *t*-test of the two groups of results verifies that there was no statistically significant difference in molecular weight between the two methods of dissolution: *t*(8) = -0.305, *P* = 0.768 > 0.05. This experiment demonstrates that the “cage stirring” method does not degrade UHMW 30 mol % APAM polymers and so is appropriate for the preparation of their solutions.

To obtain high quality light scattering data from the polymer solutions, it is necessary to use appropriate clarification techniques, most commonly filtration, to remove dust and other large particulate contaminants prior to light scattering measurements.

Table I. Replicate Analysis of a 30 mol % APAM Sample (#9)

| Sample solution (0.25 wt % in deionized water) | Stock solution (0.005 wt % in 1M NaCl) | M_w (10^6 g mol $^{-1}$) |
|--|--|--------------------------------|
| Stir bar 200 rpm 15 h | 1 | 10.6 |
| | 2 | 10.6 |
| | 3 | 11.0 |
| | 4 | 11.2 |
| | Mean (Std. dev.) | 10.9 (0.3) |
| Cage stirrer 800 rpm 1 h | 5 | 10.6 |
| | 6 | 10.6 |
| | 7 | 11.3 |
| | 8 | 12.0 |
| | 9 | 10.4 |
| | 10 | 10.8 |
| | Mean (Std. dev.) | 11.0 (0.6) |

The high viscosity of UHMW APAM solutions resulting from their UHMWs, linear structures, and, in the case of cationic or anionic copolymers or terpolymers, their ionic nature poses a challenge to such filtrations. The stock solutions of 0.1 mg mL^{-1} concentration were used in early studies. However, it was discovered that 0.1 mg mL^{-1} stock solutions were exceptionally difficult to filter with $1.2 \mu\text{m}$ filters. Because the nominal pore size of the $1.2 \mu\text{m}$ filter is much larger than the expected size of the polymer molecules, the filtration resistance suggests intermolecular entanglement at 0.1 mg mL^{-1} . When the polymer concentration was reduced to 0.05 mg mL^{-1} , little filtration resistance was experienced for the 30 mol % APAM samples with IVs up to 35 dL g^{-1} . One study by Luo *et al.*²¹ on a similar UHMW 30 mol % APAM showed that 0.05 mg mL^{-1} polymer in $1.0M$ NaCl had no shear rate dependence of viscosity and was, therefore, a dilute solution for light scattering measurement. To study the effect of filtration on polymer concentrations in solutions, total organic carbon (TOC) measurements were conducted at the authors' laboratory on several of the highest viscosity samples. Comparing the TOC data before and after filtration shows mass recoveries greater than 89%, which means a maximum 11% underestimation of MW determined by batch MALS. The combination of 0.05 mg mL^{-1} polymer concentration and $1.2 \mu\text{m}$ filtration provides good quality light scattering data and reasonable mass losses, and was, therefore, used for all polymer samples discussed in this article.

Measurement of dn/dc

The light scattering of water soluble ionic polymers, or polyelectrolytes, is more complex than that of the corresponding non-ionic polymers because of the effects of charge density in the polymer backbone. The light scattering of polyelectrolyte solutions is, therefore, usually conducted in salt solutions, such as the $1.0M$ sodium chloride used in the present work. To extend the use of light scattering theory developed for binary systems (polymer-water) to the three component system (polyelectro-

lyte-salt-water), the specific refractive index increment at constant chemical potential (rather than at constant concentration of salt) needs to be used.²⁶ To determine the specific refractive index increment at constant chemical potential, the polyelectrolyte solution needs to be fully dialyzed against the solvent until the Donnan equilibrium is reached.²⁶ Such a dialysis procedure is tedious and typically takes several days.^{16,26,27} Dialysis is not necessary when lower molecular weight polymers are analyzed with SEC because the polyelectrolytes reach Donnan equilibrium with the eluent inside the SEC columns.^{28,29} In this work, the dn/dc of 30 mol % APAM was determined with SEC/MALS analysis of three lowest MW samples #1 to #3, assuming 100% mass recovery of the analytes. The dn/dc of these samples was determined to be $0.155 \pm 0.002 \text{ mL g}^{-1}$. These results indicate that the dn/dc remains the same across the change in MW of these samples. Therefore, a dn/dc value of 0.155 mL g^{-1} was used to calculate the MW for all 30 mol % APAM samples studied in this article.

Automatic Batch MALS Measurement

In a batch MALS experiment, the scattered light intensity needs to be measured as a function of scattering angle and polymer concentration. The MALS detector automatically measures the light scattering data at multiple angles. To vary the polymer concentration, at least 5–6 solutions of different concentration need to be prepared, stirred, filtered, and injected. To simplify the process of preparing and injecting a series of different concentrations of polymer, a sample dilution and injection device was used to automatically develop and deliver a concentration gradient from concentrate. The automation hastens the analysis and likely also improves precision.

Figure 1 shows a typical representation of light scattering data: detector signal plotted against analysis time. During the analysis, the mobile phase was first injected to create a baseline. Then, a series of solutions at different polymer concentrations were injected. Finally, a mobile phase “blank” was injected once again to obtain the baseline. Each of the horizontal lines (plateaus) in Figure 1 corresponds to a single polymer concentration. In this experiment, a 10 concentration “down gradient”

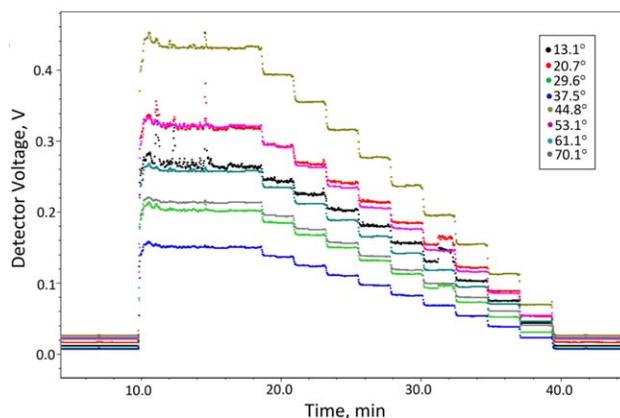


Figure 1. A typical automatic batch MALS measurement of a 30 mol % APAM sample (#7). Detector 2 to detector 9 (scattering angle 13.1° to 70.1°). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

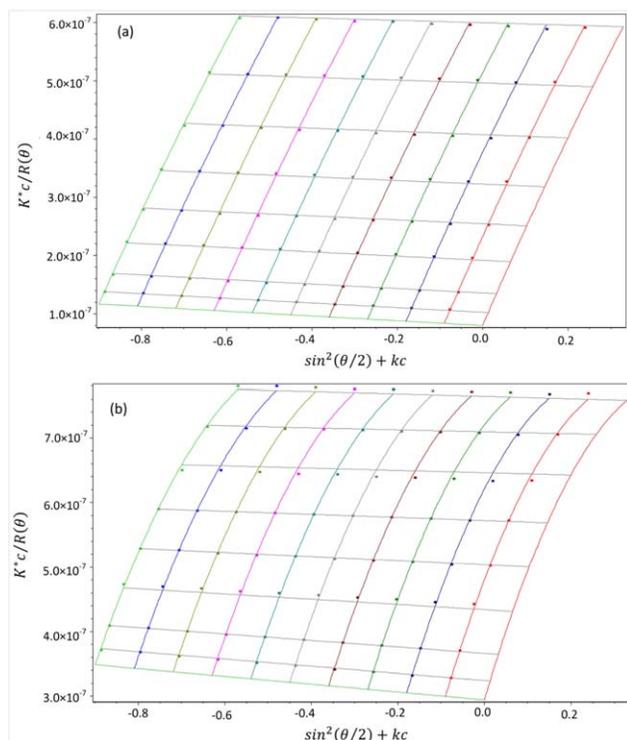


Figure 2. Comparison of (a) Zimm plot and (b) Berry plot of a 30 mol % APAM (#7). Polymer concentration: 0.05–0.005 mg mL⁻¹; scattering angles: 13.1°, 20.7°, 29.6°, 37.5°, 44.8°, 53.1°, 61.1°, and 70.1°. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

was delivered with the sample dilution and injection device described previously. During the analysis, the light scattering signal was detected simultaneously at multiple different angles. Each curve in Figure 1 corresponds to detector signals from a different scattering angle.

Data Analysis

In a batch MALS measurement, the angular and concentration dependent light scattering data are fit to the basic light scattering

equation to obtain a Zimm plot. When a Zimm Plot is constructed, there are several formalisms which can be used to fit the light scattering data and to extrapolate to zero concentration and zero angle. The most commonly used are the Zimm,³⁰ Debye,³¹ and Berry³² formalisms. They differ in the quantity used on the ordinate but the abscissa is the same in all three approaches.

Figure 2 compares the plots of a UHMW 30 mol % APAM constructed with Zimm and Berry formalisms. The Debye formalism fits the angular data poorly and is not considered for the UHMW polymers presented in this work. With a second order polynomial (the highest order available in Astra 6 software), both the Zimm and Berry formalisms fit the angular data very well and give highly reproducible results. The molecular weight and radius of gyration values determined with the Zimm model are higher than those determined with the Berry model. According to a study by Andersson *et al.*, the Berry formalism is more accurate in the determination of molecular weight for random coil polymers with radius of gyration larger than 100 nm than the corresponding Zimm formalism.³³ The authors did similar calculations on rod shaped polymer and drew the same conclusion, namely that the Berry formalism is more accurate in the determination of molecular weight than the Zimm formalism for a given polynomial order. The UHMW polymers in the present study have conformations between random coil and rod and the Berry formalism is the best model to do the extrapolations. The Berry formalism was, therefore, chosen to represent the data in this work.

It has been demonstrated that for extrapolation to zero angle, data from the higher angles are not necessary. Further, removing some of the high angle data will improve the fit at low angles, reduce errors in the extrapolation to zero angle, and thus improve accuracy in the determination of molecular weight.³³ Therefore, only the eight lowest available scattering angles from 13.1 to 70.1° were used for the analysis of 30 mol % APAM polymers.

Results of 30 mol % APAM

The automatic batch MALS method described above was used to measure the weight-average molecular weight, M_w , of a series of 30 mol % APAMs of varying MW (Table II). Along with

Table II. Intrinsic Viscosity and Weight Average MW of 30 mol % APAMs in 1M NaCl at 30 °C

| Sample | IV (dL g ⁻¹) | M_w , batch MALS ^a (10 ⁶ g mol ⁻¹) | M_w , linear ^b (10 ⁶ g mol ⁻¹) | M_w , two-equation ^c (10 ⁶ g mol ⁻¹) | M_w , quadratic ^d (10 ⁶ g mol ⁻¹) |
|--------|--------------------------|---|---|---|--|
| 1 | 4.59 | 1.22 | 1.25 | 1.25 | 1.29 |
| 2 | 6.77 | 2.23 | 2.15 | 2.15 | 2.40 |
| 3 | 9.73 | 3.46 | 3.54 | 3.54 | 3.80 |
| 4 | 13.15 | 5.31 | 5.38 | 5.38 | 5.25 |
| 5 | 22.62 | 8.61 | 11.4 | 9.12 | 8.91 |
| 6 | 29.47 | 10.5 | 16.4 | 11.5 | 11.2 |
| 7 | 30.79 | 11.4 | 17.4 | 12.0 | 11.8 |
| 8 | 35.46 | 12.6 | 21.2 | 13.5 | 13.2 |

^a Determined with batch MALS.

^b Calculated using a linear equation: $[\eta] = 1.79 \times 10^{-4} M_w^{0.723}$ dL g⁻¹.

^c Calculated using two linear equations: $M_w \leq 5.3 \times 10^6$ g mol⁻¹: $[\eta] = 1.79 \times 10^{-4} M_w^{0.723}$ dL g⁻¹; $M_w > 5.3 \times 10^6$ g mol⁻¹: $[\eta] > 13$: $[\eta] = 2.63 \times 10^{-7} M_w^{1.14}$ dL g⁻¹.

^d Calculated using a quadratic equation: $\log [\eta] = 0.341 (\log M_w)^2 - 3.63 \log M_w + 10.11$.

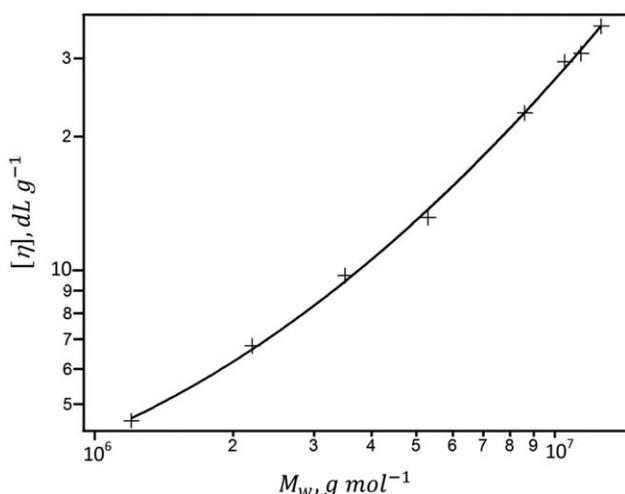


Figure 3. Plot of $[\eta]$ versus M_w of 30 mol % APAMs in 1.0M NaCl at 30 °C. Second order polynomial fit: $\log [\eta] = 0.341(\log M_w)^2 - 3.63 \log M_w + 10.11$.

intrinsic viscosity data, a plot of \log intrinsic viscosity versus \log molecular weight for 30 mol % APAMs with M_w from 1.2×10^6 to 12.6×10^6 g mol $^{-1}$ is shown in Figure 3.

The Mark-Houwink equation, $[\eta] = KM^a$, is an empirical relation and the K and a values are expected to be constant only within a limited molecular weight range.³⁴ Figure 3 shows that the Mark-Houwink relation is not linear for 30 mol % APAM in 1.0M NaCl with M_w from 1.2×10^6 to 12.6×10^6 g mol $^{-1}$. The entire molecular weight range can be fit with a quadratic relation.

$$\log [\eta] = 0.341(\log M_w)^2 - 3.63 \log M_w + 10.11 \quad (1)$$

Because of the challenges in determining MW for UHMW polyacrylamides, these types of polymers are often characterized by determining their intrinsic viscosity (IV). For practical purposes, it is desirable to provide an equation that derives MW using measured IV. Therefore, the MW and IV data determined in this work were also fit to give a power law equation [eq. (2)] to enable direct calculation of MWs from IV values.

$$\log [M_w] = 22.08 - 15.50(\log [\eta])^{-0.0773} \quad (2)$$

The intrinsic viscosity-molecular weight relationship can also be expressed by two linear equations (see Figure 4).

$$[\eta] = 1.79 \times 10^{-4} M_w^{0.723} \text{ dL g}^{-1}, \quad M_w \leq 5.3 \times 10^6 \text{ g mol}^{-1} \quad (3)$$

$$[\eta] = 2.63 \times 10^{-7} M_w^{1.14} \text{ dL g}^{-1}, \quad M_w \geq 5.3 \times 10^6 \text{ g mol}^{-1} \quad (4)$$

When the M_w is below 5.3×10^6 g mol $^{-1}$, Mark-Houwink constants $a = 0.723$, $K = 1.79 \times 10^{-4}$ dL g $^{-1}$, which are consistent with literature values that covered the similar MW regions ($< \sim 5 \times 10^6$ g mol $^{-1}$)^{35–37} (see Table III). When the M_w is above 5.3×10^6 g mol $^{-1}$, Mark-Houwink constants $a = 1.14$, $K = 2.63 \times 10^{-7}$ dL g $^{-1}$, are significantly different from those values for the lower MW range.

The batch MALS experiments were conducted at room temperature without temperature control. The MALS cell temperature

fluctuates within 28 ± 2 °C. According to literature,³⁴ both constant k and a are insensitive to temperature when a exceeds about 0.70, and they can be used in a ten-degree range on either side of temperature at which the constants were determined. Since a constants for the 30 mol % APAMs determined in this and a few other work^{35–37} are greater than 0.70, the constants determine in this work are suitable for use at 25–30 °C, at which most IV measurements on polyacrylamides are conducted.

The value of k is affected by the molecular weight distribution (MWD) of the polymer samples used to determine it. The Polymer Handbook³⁴ shows the impact of MWD on the constant k and lists the correction factors for k of poly-dispersed samples ($M_w/M_n > 1$) relative to that of the mono-dispersed sample ($M_w/M_n = 1$). Mark-Houwink equations are often determined using narrowly dispersed polymers and the k constant can be corrected for poly-dispersed samples using the correction factors provided in the Polymer Handbook. The polymers used in this work were made via conventional free-radical polymerization, which is commonly used in industry to manufacture commercial polyacrylamide or its copolymers despite the resultant high polydispersity. Compared to the k constant determined with narrowly dispersed polymer samples, the Mark-Houwink constants presented in this work are more applicable to industrial polymers that often have broad MWD. In addition, calculations using the correction factors indicate that when the difference in polydispersity index between the polymer of interest and the reference polymers used to determine the k constant is less than two fold, assuming an a value of 0.70 or higher, the error in determination of M_w resulting from neglecting a polydispersity is less than 7% for exponential type MWD and 10% for Log Normal type MWD, which are acceptable for most practical applications. Therefore, poly-dispersed polymers were used without fractionation in the work described herein.

The Mark-Houwink exponent a is related to polymer conformation in solution. For flexible polymers in a good solvent, a is

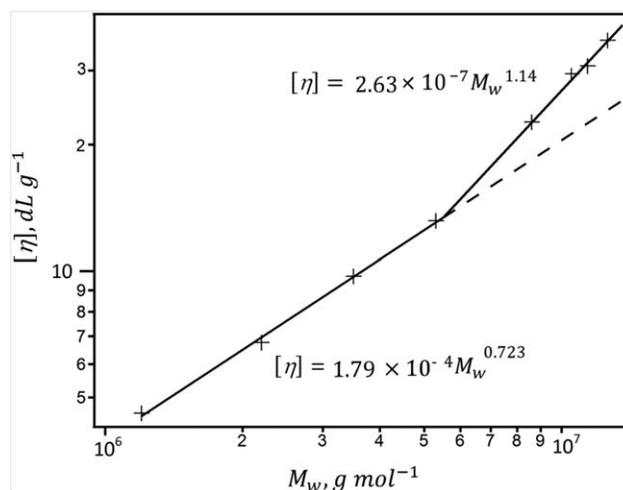


Figure 4. Mark-Houwink relation of 30 mol % APAM in 1.0M NaCl at 30 °C: $M_w \leq 5.3 \times 10^6$ g mol $^{-1}$, $[\eta] = 1.79 \times 10^{-4} M_w^{0.723}$ dL g $^{-1}$; $M_w \geq 5.3 \times 10^6$ g mol $^{-1}$, $[\eta] = 2.63 \times 10^{-7} M_w^{1.14}$ dL g $^{-1}$.

Table III. Comparison of Literature K and a Values of Acrylic Acid (AA)/Acrylamide (AM) Copolymers

| Authors | Composition | Solvent | T (°C) | K (dL g ⁻¹) | a | MW ^a range | Reference |
|------------------------|-------------|--------------------------------------|----------|---------------------------|-------|--------------------------------|-----------|
| Wu <i>et al.</i> | 30 mol % AA | 0.2M Na ₂ SO ₄ | 25 | 2.22×10^{-4} | 0.742 | $0.01\text{--}1.2 \times 10^6$ | 35 |
| Klein <i>et al.</i> | 30 mol % AA | 0.5M NaCl | 25 | 7.0×10^{-4} | 0.68 | $0.77\text{--}5.5 \times 10^6$ | 36 |
| McCarthy <i>et al.</i> | 20 mol % AA | 1M NaCl | 25 | 1.41×10^{-4} | 0.744 | $0.1\text{--}3.0 \times 10^6$ | 37 |
| Wang <i>et al.</i> | 30 mol % AA | 1M NaCl | 30 | 1.79×10^{-4} | 0.723 | $1.2\text{--}5.3 \times 10^6$ | This work |
| | | | | 2.63×10^{-7} | 1.14 | $5.3\text{--}12.6 \times 10^6$ | |

^aDetermined by light scattering.

observed to be between 0.5 and 0.8.^{34,38} For hyper-branched polymers, the a value can be lower than 0.5. For rigid polymers, the a value can be higher than 1 with a rigid rod having a theoretical a value of 2.³⁹ When the M_w is between 1.2×10^6 to 5.3×10^6 g/mol, the a parameter of the 30 mol % APAM is equal to 0.723 which is within the indicated range of 0.5–0.8 for flexible polymers in a good solvent. When M_w is higher than 5.3×10^6 g/mol, the $\log[\eta]$ versus $\log M_w$ plot begins to exhibit upward curvature and a higher a value of 1.14 is determined, indicating a larger excluded volume and a more extended conformation.⁴⁰

Other factors which could cause deviation from linearity of the Mark-Houwink relation include branching at higher MW or lower measured IV values for UHMW polymers as a result of shear degradation during the measurement. These factors, however, would have resulted in a downward curvature instead of an upward one in the $\log[\eta]$ versus $\log M_w$ plot and are, therefore, not the causes of the non-linear relation observed in this work. Similar nonlinear Mark-Houwink relations have been observed for poly(methyl methacrylate)⁴¹ and polystyrene⁴² over a wide MW range. The author in these instances attributed the change in the value of the exponent a with molecular weight to the differences in permeability of the polymer coil to the flow streamlines.³⁹

One practical consequence of a non-linear Mark-Houwink relationship is that the MW is significantly overestimated if the Mark-Houwink equation obtained with lower MW polymers is applied in the UHMW range. Table II compares the MWs of the 30 mol % APAMs calculated using three different Mark-Houwink relations: a linear equation for the lower MW region with linear extrapolation to UHMW region, two separate linear equations for $M_w \leq 5.3 \times 10^6$ g mol⁻¹ and $M_w > 5.3 \times 10^6$ g mol⁻¹, and a quadratic equation that covers the entire MW range. The results show that the quadratic fit and two-equation linear fit give results similar to those determined with batch MALS. For 30 mol % APAM polymers with M_w greater than 5.3×10^6 g mol⁻¹, the MWs calculated by linear extrapolation of the low MW equation to high MW region are significantly higher than the values obtained with batch MALS measurements and the other two fit models. Comparison of the third and fourth columns in Table II shows that the higher the IV or MW values, the larger the discrepancy in MW determined with the two approaches. For the highest IV sample, sample #8, the MW determined with batch MALS is 12.6×10^6 g mol⁻¹ and the MW predicted with linear extrapolation of the low MW

equation is 21.2×10^6 g mol⁻¹, a 68% overestimation. This comparison demonstrated that the linear extrapolation approach widely used in the industry today significantly overestimates the MW of UHMW polymers

CONCLUSIONS

A batch mode MALS method was developed and optimized to determine the MW of UHMW PAM polymers. The MALS detector was combined with an automatic sample dilution and injection device to automatically deliver a concentration gradient of polymer from a stock solution. The automation makes it practical to use the batch MALS method for routine analysis of UHMW PAM polymers. The automatic batch MALS method was used to measure the weight-average molecular weight, M_w , of a series of 30 mol % APAMs of differing MW. A $\log[\eta]$ versus $\log M_w$ relation for 30 mol % APAM with M_w in the range of 1.2×10^6 to 12.6×10^6 g mol⁻¹ was established. The results from these experiments show that the Mark-Houwink relation for 30 mol % APAM in 1.0M NaCl is non-linear. To the best of the authors' knowledge, this is the first time that the Mark-Houwink relation was determined for a 30 mol % APAM covering the UHMW ($>5 \times 10^6$ g mol⁻¹) region. The non-linear Mark-Houwink relationship suggests that the current practice of using a linear extrapolation of Mark-Houwink equation determined with lower MW APAM to UHMW regions likely significantly over-estimates the MW of UHMW APAM polymers. Quadratic or two-equation linear fits should provide a more accurate Mark-Houwink relationship for 30 mol % APAM and related similar polymers.

In this article, the automated batch MALS method was used to study 30 mol % APAMs. The method is also suitable for the MW characterization of UHMW acrylamide homopolymer and copolymers of various other compositions. Furthermore, it can be potentially used to analyze any UHMW biopolymers and synthetic polymers, providing accurate MW values that are critical to correlations with their efficacy in various industrial applications.

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