Physicochemical study of polyelectrolytes containing $–AsO(OH)_2$ and $–AsO(ONa)_2$ groups by SEC-MALS

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1. Abstract

Polyelectrolytes present challenges for their study in size-exclusion chromatography (SEC) due to expansion or contraction effects and possible excessive retention in the column leading to erroneous molar mass distributions. SEC combined with multiangle light scattering (MALS) detection is employed for the characterization of polymers from the o-methacryloylaminophenylarsonic acid and its sodium salt form at different pH. Absolute molar mass, size distribution and root mean square radius of the polymer are being obtained to study the effect of pH on the retention process of the sample. From the molar mass and radius, the conformation of the polymer can be deduced. This way, the change in polymer conformation with a change in pH will be analyzed.

2. Introduction

Size-exclusion chromatography (SEC) is a widely used chromatographic technique for the separation of macromolecules based on the difference in their sizes [1]. When SEC is used for the characterization of polyelectrolytes (macromolecules bearing electric charges on the chain), it becomes challenging due to the nature of these materials. Polyelectrolytes in solution tend to expand or contract as the pH or the ionic strength changes due to changes in the number of charged sites or changes in the concentration of the counter ions. Using SEC, a change in the size of the polymer will change its retention time and thus its apparent molar mass. One can minimize that problem by adding salt which screens these charges and thus decreases the expansion of the polymer chain. Another problem is the ion inclusion/exclusion the could occur between the polyelectrolyte and the SEC column packing. Since the packing material is charged, polymers of the same charges will be repelled and polymers of opposite charges will be retained, introducing distortions in the molar mass distribution if analized by an exthernal calibration method. The accurate characterization of polyelectrolytes can be achieved using multiangle light scattering (MALS) detection coupled with a SEC system. Since MALS is an absolute technique, molar masses are determined independent of retention time [2].

The ability of light scattering techniques to determine the radius of the macromolecules is of great importance for the determination of molecular conformation (spherical, random coil, rigid rod). To be able to know how the conformation of the polyelectrolytes changes with the pH or ionic strength is important for a better understanding of the polyelectrolyte behaviour. In this study we employ SEC-MALS for the characterization of polymers from the *o*-methacryloylaminophenylarsonic acid (*o*-MAPHA) and its sodium salt (*o*-MAPHA-Na) form at different pH.

3. Experimental section

Preparation of monomer *o*-MAPHA, its sodium salt *o*-MAPHA-Na and their free radical polymerization have been described previously [3,4]. Diluted solutions (~10 mg/mL) of the polymers from *o*-MAPHA in DMF and from *o*-MAPHA-Na in water at pH = 7 and pH = 4 were prepared.

The dn/dc (refractive index increment as a function of molecular concentration) of the solutions was determined off-line using a Refractive Index Detector (Optilab rEX, Wyatt Technology Corp.) at 690 nm. These values are necessary for the measurement of molar mass in SEC-MALS.

The SEC-MALS of the polyelectrolyes using mobile phases at different pH was carried out at ambient temperature (25^0C) The multiangle light scattering detector was a 8-angle Dawn Heleos (Wyatt Technology Corp.) operating at a wavelength of 658 nm. After data treatment using ASTRA software (Wyatt Technology Corp.), the SEC-MALs technique provided the weight average molecular weight (M_w) number average molecular weight (M_n), polydispersity index (PDI) and rms radius.

4. Results and discussion

The dn/dc value for the polymer from the o-MAPHA-Na in the pH = 7 mobile phase was 0.170 mL/g. The SEC-MALS for this polyelectrolyte in this mobile phase yielded the following results:

$M_w = 1.548 \times 10^6$ g/mol

$M_n = 1.125 \times 10^6$ g/mol

PDI = 1.376

rms = 54.5 nm

Figure 1 shows the distribution analysis (Cumulative weight fraction y differential weight fraction distributions) obtained from this SEC-MALS.

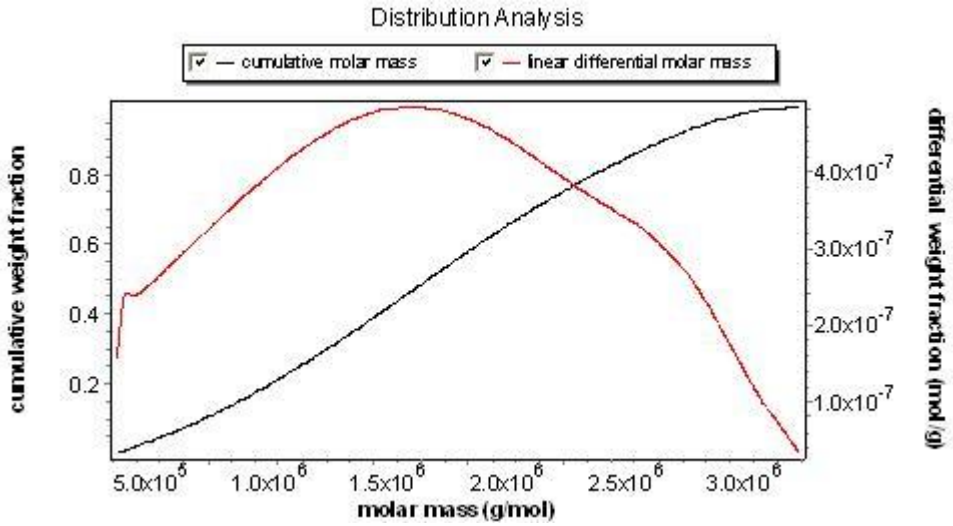

Figure 1. Cumulative and differential molecular weught distribution for the poly(o-MAFA-Na) at pH = 7.

Figure 2 shows the plot of the mean square radius (rms) versus retention time. There is an almost linear decrease in the value of the rms, which is an indication that the retention mechanism in the chromatographic column is based on the "size" of the polyelectrolyte and that significant portions of the polymer are not reatined on the column due a interactions with the column packing.

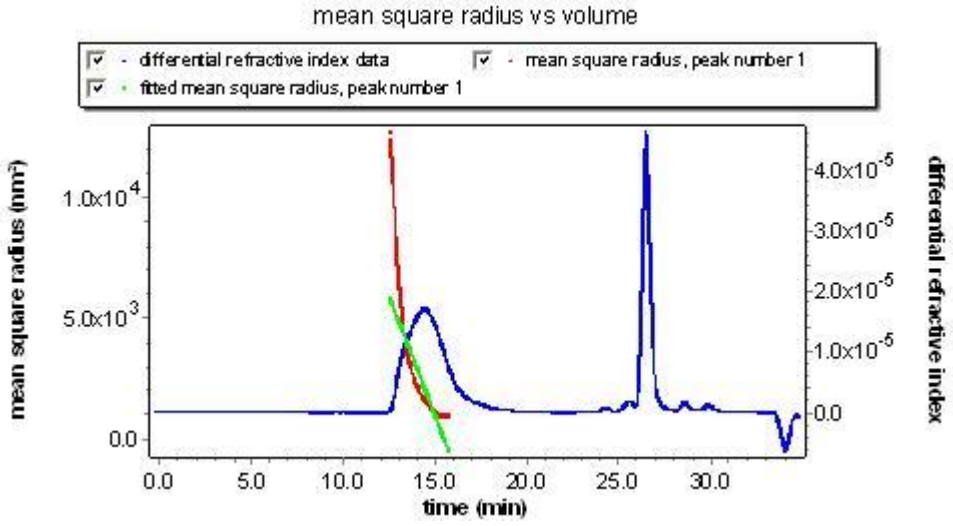

Figure 2. Plot of rms radius vs. Retention time for the poly(o-MAFA-Na) at pH = 7.

A log-log plot of the radius versus molar mass will allow to infer the conformation of the polyelectrolyte at a given pH, because the slope of a such plot is related to the shape of the polymer. We are analyzing the data obtained from the SEC-MALS of the polyelectrolytes mentioned to have knowledge of how the conformation changes with changes in the pH.

5. Conclusions

The characterization of polyelectrolytes from the *o*-methacryloylaminophenylarsonic acid (*o*-MAPHA) and its sodium salt (*o*-MAPHA-Na) at different pH is being performed by SEC-MALS. The data obtained will allow us to determine the conformation of the macromolecules in solution and to have a better understanding of the behaviour of these polyelectrolytes with changes in the pH.

6. References

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