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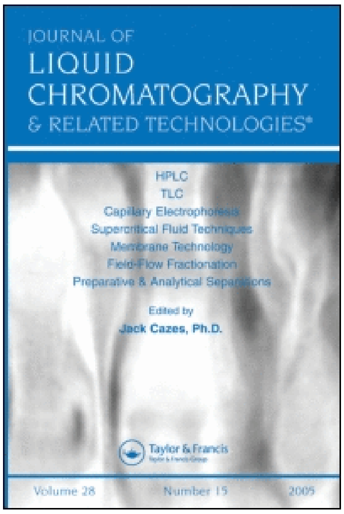

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A pH Effect in the HPSEC Separation of Polyacrylamide-Based Copolymers

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A pH EFFECT IN THE HPSEC SEPARATION OF POLYACRYLAMIDE-BASED COPOLYMERS

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ABSTRACT

Four polyacrylamide-based samples, having the same nominal molecular weight and molecular weight distribution, have been characterized by HPSEC using two column sets and a mobile phase of phosphate buffer. Depending upon the pH, the separations demonstrate that the systematic differences between samples are influenced by the level of anionic sites along the polymer chain. It is found that the HPSEC elution profiles of these samples are reversed when the pH is changed from 2.2 to 7.0. The anionicity of the samples ranges from less than 0.5 mole % carboxyl content (the homopolymer of acrylamide) to 33.0 mole %.

Capillary viscometry data support these findings in the two solvent media, indicating that no adsorption effects prevail in the chromatography. Static and on-line low angle laser light scattering (LALLS) data on the homopolymer of acrylamide also suggest that no adsorption or degradation is occurring in the chromatographic process.

INTRODUCTION

High molecular weight polymers of poly(acrylamide) (PAM) and its copolymers are used as mobility control agents in tertiary oil recovery, paper filler retention aids, and as flocculants in many water clarification processes. The

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solution properties (a reflection of the hyrodynamic volume or size in solution) of such polyelectrolytes are affected by the solvent media in which they are dissolved. As reported in the literature(1-6), it is well established that ionic strength, solvent and pH have a marked effect on polymer conformation.

For high molecular weight polyelectrolytes, the characterization by high performance size-exclusion chromatography (HPSEC) and data interpretation are complicated by: 1) the presence of ionic charges and their distribution on the polymer chains in addition to 2) the major effect of molecular weight (MW) and molecular weight distribution (MWD). Both fundamental properties contribute to the effective hydrodynamic volume of a macromolecule in solution - the basic separation parameter of HPSEC. As a result, the effects of MW and various polymer-solvent interactions have been difficult to demonstrate(7).

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This report describes a brief chromatographic study of four polyacrylamide-based samples having the same nominal molecular weight and molecular weight distribution and different levels of anionic content. The samples are examined in two column systems under conditions where the ionic nature of these polymers plays a dominant role in the solution properties. This unique set thus permits one to study the effect of anionicity by HPSEC in different solvent media, without complications due to significant MW or MWD differences. Some of these results have been documented in a summary report for an NSF grant(8).

EXPERIMENTAL

The three copolymer samples were prepared by alkaline hydrolysis from the same homopolymer ("S-88") of acrylamide . Conditions were carefully selected and controlled to minimize molecular weight degradation(8). This has been shown to be feasible by Muller and co-workers(9). The % anionic level (or "anionicity") of these samples ranges from less than 0.5

mole % (for the "neutral" homopolymer) to 33 mole % carboxyl content, as measured by titrimetry.

The mobile phase used throughout this work was 0.1M NaH_2PO_4 and 0.3M Na_2SO_4, with dilute H_3PO_4 used to adjust the pH to either 2.2 or 7.0 units. The ionic strength (μ) is about 1.0 M. All solvents and polymer solutions were filtered prior to use through glass fiber filters (Whatman Labsales, Hillsboro, OR, Grades GF/D and GF/F). A modular chromatography system (Waters Associates, Milford, MA) consisting of a Model M6000A pump, a WISP Model 710B automatic injector, and a Model 401 differential refractive index (DRI) detector was used for the work at pH = 7.0. Data collected at a pH of 2.2 utilized UV detection at 206 nm with a SpectroMonitor III variable-wavelength detector (LDC Analytical, Riviera Beach, FA).

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One column set included four TSK/PW® type columns (Varian, Walnut Creek, CA) having pore size designations of 6000PW®, 5000PW®, 4000PW®, and 2000PW®. With this column set, the pH of the mobile phase was 2.2. 400 μL injections of each polymer solution were made at nominal polymer levels of 0.1% (wt/vol). All filtered solutions were injected two hours after dissolution with run times of 100 minutes and a flow rate of 0.5 mL/min. With this system, the UV detector was set at 0.2 AUFS.

The second column set consisted of three μBondagel® columns (Waters Associates, Milford, MA) connected in series. The pore sizes are designated as E-High A, E-1000, and E-500. This set was used with the same mobile phase noted above, but at a pH = 7.0. In this separation, a set of polystyrene sulfonate standards (Pressure Chemical Company, Pittsburgh, PA) was used for calibration since polyacrylamide standards were not available at the time. These standards ranged in molecular weight (MW) from MW = 6.5×10^3 to MW = 1.2×10^6 g/mole.

All data were collected and analyzed on a Hewlett Packard Laboratory Automation System (LAS) 1000 Series computer (HP 3354) using software developed in-house. The data transfer rate was 0.5 Hz.

Light scattering data were obtained with a low angle laser light scattering (LALLS) photometer (Model KMX-6, LDC Analytical, Riviera Beach, FL). Static measurements were made to determine the weight-average molecular weight (M_w) and the second virial coefficient A_2. A dn/dc value of 0.16 mL/g was used as the optical constant for the mobile phase at pH = 2.2. The same TSK/PW® column set with phosphate buffer (at pH = 2.2) was also used to determine the molecular weight distribution with on-line LALLS detection. Data were processed using MOLWT3 software (LDC Analytical) on a DEC Micro/PDP 11 computer.

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RESULTS AND DISCUSSION

In the phosphate buffer system at pH = 2.2, the static light scattering data indicate $M_w = 6.64 \times 10^5$ g/mole (and $A_2 = 2.35 \times 10^{-4}$ mole-cm/g^2) for the homopolymer sample (S-88). From the on-line LALLS analysis with the set of TSK/PW® columns, one finds $M_w = 6.07 \times 10^5$ and $M_w/M_n = 1.62$. This good agreement between static LALLS and HPSEC/LALLS for M_w is an indication that the chromatographic system has little or no effect upon the polymer. Thus degradation and/or adsorption is probably minimal in this separation, and a true size separation mechanism probably prevails. The DRI and LALLS responses are shown in Figure 1 as a function of data point and time respectively. No exclusion of polymer is evident.

The separations observed with the TSK/PW® columns in the phosphate buffer mobile phase at pH = 2.2 are shown in Figure 2. It is apparent that higher anionicity results in size distributions which have shifted uniformly to lower elution times. Apparently, the copolymers with higher carboxyl content have a more compact hydrodynamic volume. The

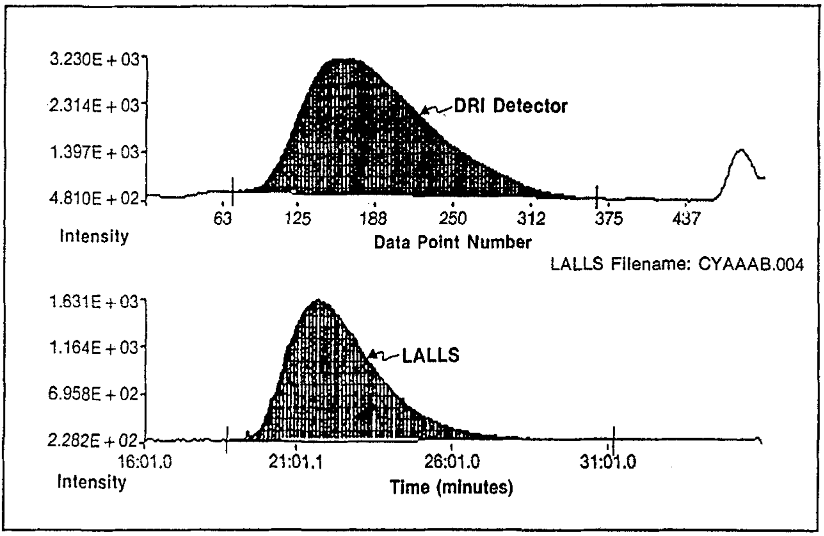

FIGURE 1. HPSEC/LALLS Chromatograms of Poly(acrylamide) S-88.

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separation between samples may be a result of intramolecular carboxyl-dimer formation. Such intramolecular hydrogen bonding has been noted in organic systems(**10**).

In the same mobile phase with the μBondagel® columns and at a pH = 7.0, the elution behavior between samples is **reversed** (not shown). Under these conditions, the homopolymer now exhibits the smallest hydrodynamic volume or size and elutes **later** than the samples having higher carboxyl content. Thus the copolymers exhibit a more extended conformation in solution relative to the more neutral homopolymer, as one may expect at this pH.

Figure 3 illustrates these data after applying the calibration with polystyrene sulfonate standards. At higher carboxyl levels, it is apparent that the separation is better with the TSK/PW® set due to the availability of larger pores

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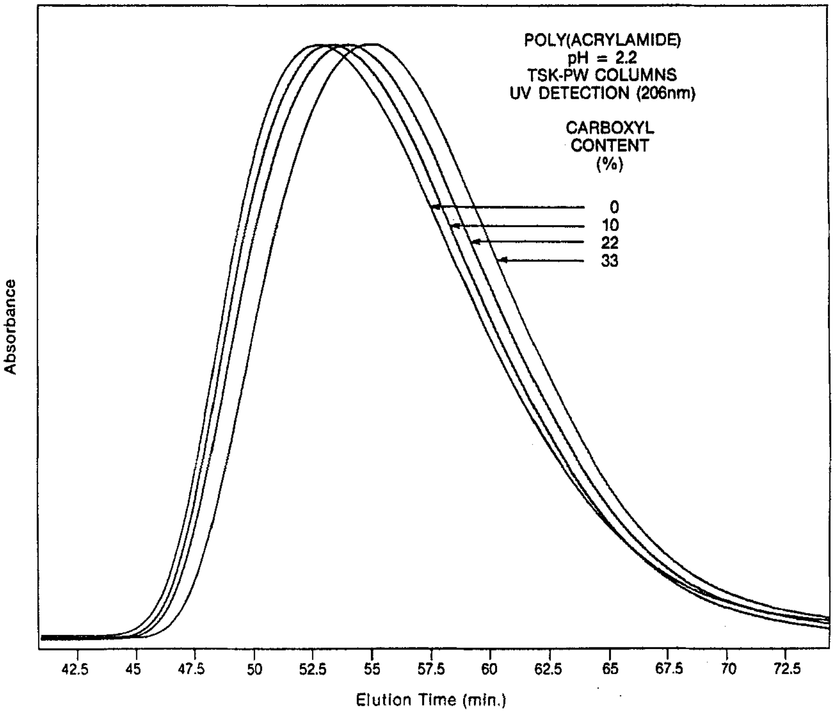

FIGURE 2. HPSEC Chromatograms of Four Poly(acrylamides) of Varying Carboxyl Content at pH = 2.2.

relative to the μBondagel® column set. The calculated relative molecular weight moments of the distribution, based upon polystyrene sulfonate, are shown in Table 1. These relative data are not very different from the absolute data derived with the on-line LALLS experiment.

Intrinsic viscosities at each pH in the phosphate buffer are summarized in Table 2. The trends in the data concur with the observed HPSEC separations. As shown by the chromatographic separations, it is apparent that the trends in molecular size indicated above are also observed without a column system. This implies that the chromatographic separation system is well-behaved. At equivalent molecular

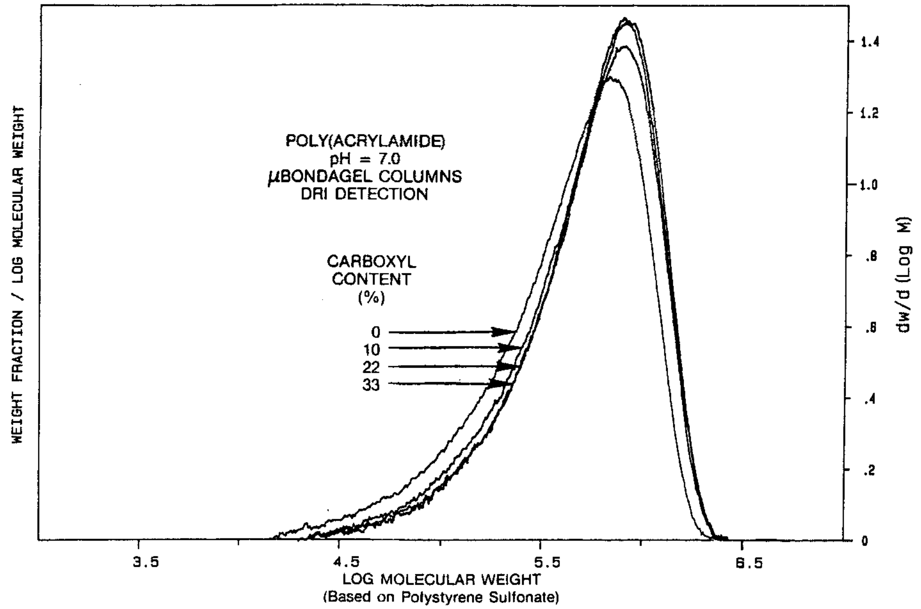

FIGURE 3. Relative MWDs of Four Poly(acrylamides) of Varying Carboxyl Content at pH = 7.0, based on Polystyrene Sulfonates.

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weights, the ratio of intrinsic viscosities is a good approximation to the ratio of effective hydrodynamic volumes, and the differences seen in this work are very likely due only to size differences.

It is interesting to note that comparable results were reported by Langhorst(11) and co-workers using hydrodynamic chromatography (HDC) with higher MW and partially hydrolyzed PAMs (as in the present study). This team observed similar chromatographic separations at a pH of 8.4 and a corresponding increase of sample viscosities with extent of hydrolysis of the PAM. At the same ionic strength ($\mu \sim 0.1$ M) and a pH of

TABLE 1.

MOLECULAR WEIGHT MOMENTS

(Based on Polystyrene Sulfonate Standards)

	M_w	M_n
	<--------x10^{-5}-----------> (g/mole)	
Sample		
S-88	5.4	2.5
S-62	6.3	3.3
S-63	6.7	3.6
S-64	6.6	3.5

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TABLE 2.

INTRINSIC VISCOMETRY DATA

pH	2.4	7.0
	<---------(dL/g)---------->	
Sample		
S-88	2.49	2.18
S-62	1.80	2.79
S-63	1.42	3.82
S-64	1.14	4.21

4.0 however, no differentiation in the HDC elution profiles was reported and viscosities were also not significantly different. Compared with the data reported here, the distinctions may be accounted for by a tenfold difference in MW of the PAMs, a tenfold difference in the ionic strength of the solvents used, a lower pH in the present study, and/or differences in the relative sensitivities of the chromatographic techniques. Further work is needed to clarify this point.

At a low pH of 2.2, the observation that HPSEC profiles shift to higher elution time with increasing anionicity is in accord with the better flocculation performance of nonionic PAMs for acidic substrates(12). This conforms with the concept that molecular size is an important fundamental parameter in flocculation.

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