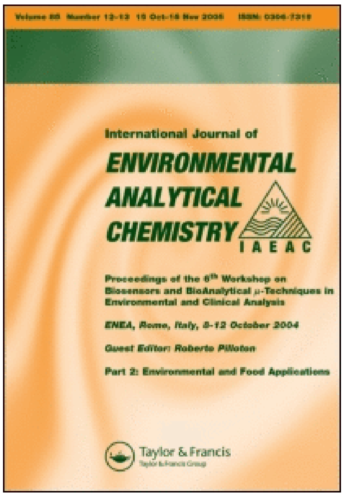

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T. Soponkanaporn[a]; R. Gehr[a]
[a] Department of Civil Engineering and Applied Mechanics, McGill University, Montreal, Quebec, Canada

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Quantitative Determination and Peak Molecular Weight Analysis of Acrylamide-based Polyelectrolytes by Size Exclusion Chromatography

T. SOPONKANAPORN and R. GEHR

Department of Civil Engineering and Applied Mechanics, McGill University, Montreal, Quebec, H3A 2K6, Canada

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High molecular weight cationic, anionic and non-ionic acrylamide-based polyelectrolytes at low concentrations were determined quantitatively by using size exclusion chromatography (SEC). A series of columns containing macroporous silica particles coated with polyamine (Synchropep Catsec) was used together with a UV detector at 200 nm. An aqueous solution of KH_2PO_4 was used as the mobile phase to control the non-size-exclusion mechanisms. Applications of SEC in the study of cationic polyelectrolyte degradation by ozone and in the trace analysis of cationic polyelectrolyte in the presence of high salt concentration are also illustrated.

KEY WORDS: Polyelectrolytes, size exclusion chromatography.

INTRODUCTION

Acrylamide-based polyelectrolytes are widely used as coagulants or coagulant aids in paper, water and sewage treatment industries, and for mobility control in the oil industry, due to their unique ability to form non-toxic water soluble polymers of high molecular weights[1]. They are used in either nonionic (e.g. polyacrylamide), anionic (e.g.

partially hydrolysed polyacrylamide), and cationic (e.g. copolymer of acrylamide and dimethyl-amino-ethyl acrylate quaternized with methyl chloride) forms. The last mentioned is increasingly used in water and sewage treatment[2] because colloids in natural systems are generally negatively charged.

Several methods had been developed to characterise the acrylamide-based polylectrolytes, namely viscosity, light diffraction[3], turbidity[4], bromine oxidation[5], Kjeldahl nitrogen[6], base hydrolysis[7], colloid titration[8], luminescence titration[9], spectrophotometry[10] and spectrofluorometry[11]. Size exclusion chromatography (SEC) is commonly used to determine the molecular weight and molecular weight distribution of polymers. It has also been used to detect trace amounts of anionic partially hydrolysed polyacrylamide[12] because it is relatively immune to interferences which affect most of the above methods. However, SEC of high molecular weight cationic polyelectrolytes is quite problematic due to the adsorption of charged polymers to the column packing. Suitable commercially available packings for SEC of very high molecular weight cationic polyelectrolytes have been developed only recently[13,14].

This paper reports on the use of SEC to determine the peak molecular weight of fresh and reacted acrylamide-based polyelectrolytes of high molecular weights, as well as to determine the concentrations of cationic, anionic and nonionic polyelectrotrolytes in an aqueous salt solution.

EXPERIMENTAL

Apparatus

The analytical system consisted of a Waters (Milford, Mass.) 840 data and chromatography control station, a Waters 510 pump operated at 2 mL/min, a Rheodyne (Berkeley, CA) 7125 injection valve fitted with a 200 or 1000 μL sample loops and a Waters Lambda-Max LC spectrophotometer set at a wavelength of 200 nm. The columns (600 mm × 7.8 mm i.d.) were stainless steel and dry-packed with Synchroprep Catsec 10,000 and 1,000 obtained from Synchrom, Inc. (Linden, Ind., USA). The mobile phase was 0.25 M KH_2PO_4 adjusted to pH 3 with H_3PO_4.

Materials

Commercial cationic copolymers of acrylamide and dimethyl-aminoethyl acrylate quaternized with methyl chloride, and anionic partially hydrolysed polyacrylamide, were kindly supplied by Allied Colloids Ltd. (Bradford, England) and Stockhausen Ltd. (Krefeld, Germany). Non-ionic polyacrylamides were obtained by ammonolysis of the above cationic polyelectrolytes. The polyelectrolytes used in this study are listed in Table I.

Table I Polyelectrolytes used in this study.

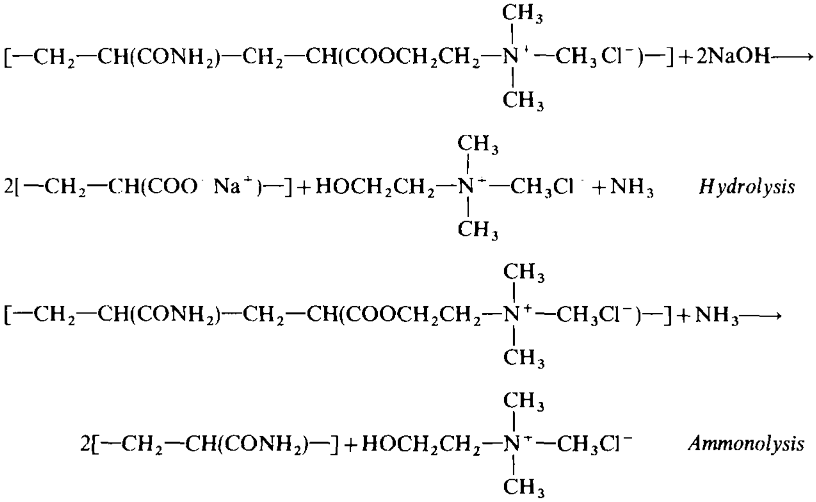
		$\bar{M}$v (in million)			
Type	% Charge by wt.	Hydrolysis	Ammonolysis	Viscometry	Manufac. literature
Cationic					
2317/1	80	1.85	1.62		
2317/3	80		5.88		
2318/1	50	1.61	1.47		
2318/2	50	2.97	3.48		
2318/3	50	4.77	4.75		
2319/1	20	0.95	0.76		
2319/4	20	2.07			
Polymer A	63	4.55	5.55		
2395	60				8.45
Anionic					
Percol 727	30				ultra high
Non-ionic					
N 2318/1	—			1.00	
N 2318/2	—			2.38	
N 2318/3	—			3.25	
NA	—			5.55	

The viscosity averaged molecular weights ($\bar{M}$v's) of cationic copolymers were determined indirectly by both base hydrolysis and ammonolysis, which convert the cationic copolymers into homopolymers of polyacrylate or polyacrylamide respectively. The $\bar{M}$v's were then determined viscometrically from the following [η]-MW relationships:

$[\eta]=0.42\times10^{-3}M^{0.66}$ in 2 M NaOH at 25°C for polyacrylate[15],

$[\eta]=3.73\times10^{-3}M^{0.66}$ in 1 M $NaNO_3$ at 30°C for polyacrylamides[16].

The $\bar{M}v$'s obtained were then converted back to the original cationic copolymers according to the stoichiometric equations of hydrolysis or ammonolysis reactions, as follows:



$$[-CH_2-CH(CONH_2)-CH_2-CH(COOCH_2CH_2-\overset{CH_3}{\underset{CH_3}{N^+}}-CH_3Cl^-)-]+2NaOH\longrightarrow$$

$$2[-CH_2-CH(COO\ Na^+)-]+HOCH_2CH_2-\overset{CH_3}{\underset{CH_3}{N^+}}-CH_3Cl\ +NH_3 \qquad \textit{Hydrolysis}$$

$$[-CH_2-CH(CONH_2)-CH_2-CH(COOCH_2CH_2-\overset{CH_3}{\underset{CH_3}{N^+}}-CH_3Cl^-)-]+NH_3\longrightarrow$$

$$2[-CH_2-CH(CONH_2)-]+HOCH_2CH_2-\overset{CH_3}{\underset{CH_3}{N^+}}-CH_3Cl^- \qquad \textit{Ammonolysis}$$

Viscosity determination

Viscosities were determined at 25°C with a standard Ubbelohde capillary viscometer.

RESULTS AND DISCUSSION

Selection of mobile phase

Since polyacrylamide shows maximum absorption of UV light at a wavelength of 192.5 nm[10], the UV detector set at its minimum wavelength of 200 nm was used. An aqueous solution of KH_2PO_4, which is nearly transparent at this wavelength, was used as a mobile phase to prevent non-size-exclusion mechanisms (ion inclusion, ion exclusion, adsorption) and to control the polyelectrolyte's hydrodynamic volume. The mobile phase was also adjusted to pH 3 to suppress the dissociation of silanol groups and therefore prolong the column life and prevent adsorption. The salt concentrations usually used in SEC for cationic polymers varied from 0.05 to 2.0 M. Levy and Dubin[17] suggested a minimum concentration of 0.1 M NaCl for every 0.2 mg of polymer injected. Barth[18] suggested using a salt concentration at which the intrinsic viscosity approaches a constant value, and where the polyelectrolyte contraction is maximum. Polymer concentrations generally used in SEC studies are high (above 100 mg/L) and in the useful working range of intrinsic viscosity measurement. On the other hand, polymer concentrations usually used in water and wastewater treatment are much lower (below 100 mg/L), and too high a salt-to-polymer ratio could lead to an additional retention volume due to adsorption through a reversed charge effect and/or a hydrophobic (salting out) mechanism[3]. The appropriate salt concentrations were therefore determined experimentally. The viscosity indices (or reduced viscosities), η_c, instead of intrinsic viscosities, were measured at different salt concentrations. The value of η_c decreased with increasing salt concentrations (Figures 1 and 2), which is typical for polyelectrolytes, and leveled off at high salt concentrations at which the polyelectrolyte contraction is maximum. The appropriate salt concentrations required depended on the polymer concentration (Figure 1), molecular weight and cationic charge density of the polymers (Figure 2). The higher these amounts, the higher the salt concentrations required.

Analysis of cationic acrylamide based polyelectrolytes

Limits of detection Analysis of polymer A at the appropriate salt concentration obtained from the previous measurements (0.25 M) showed a linear response from 5–100 mg/L, with reasonably consistent retention times (Figure 3 and 4). The second peak, at about 22 minutes, may be either low molecular weight impurities usually found in commercial polyelectrolytes, or an artifact of the ionic system, or both.

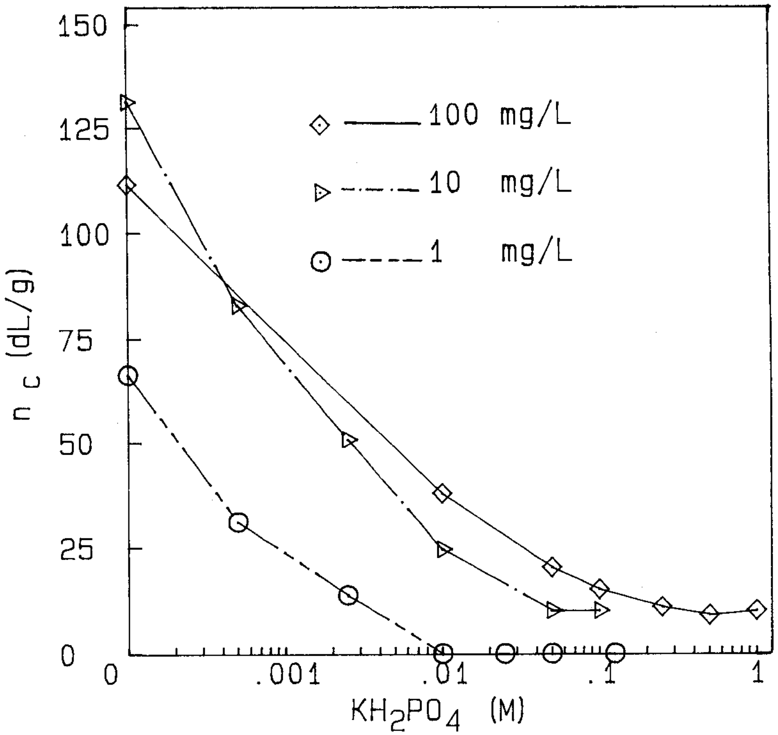


Figure 1 Effect of ionic strength on the viscosity index of polymer A at various concentrations.

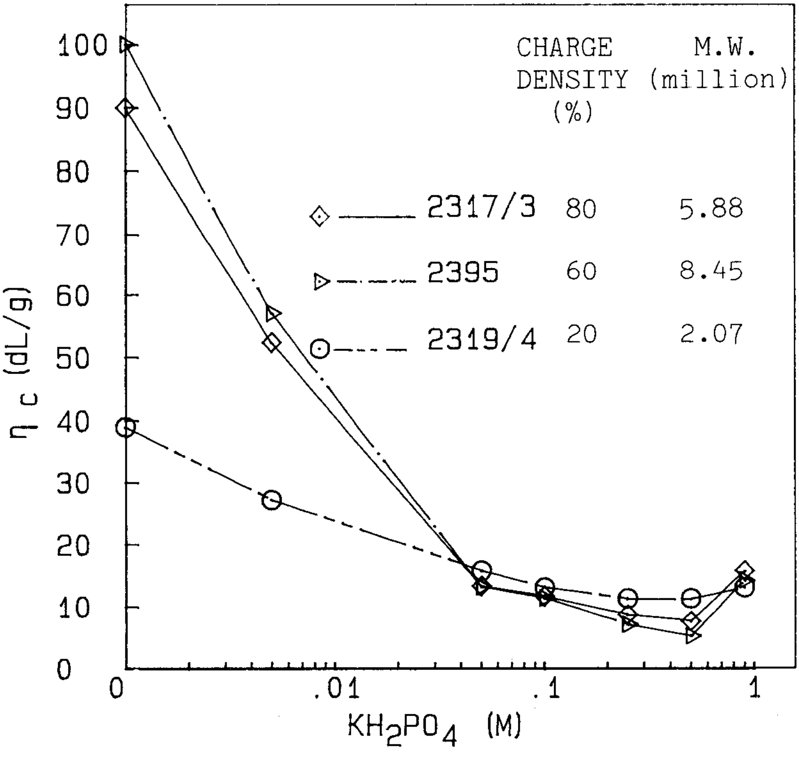


Figure 2 Effect of ionic strength on the viscosity index of various cationic polyelectrolytes at 100 mg/L.

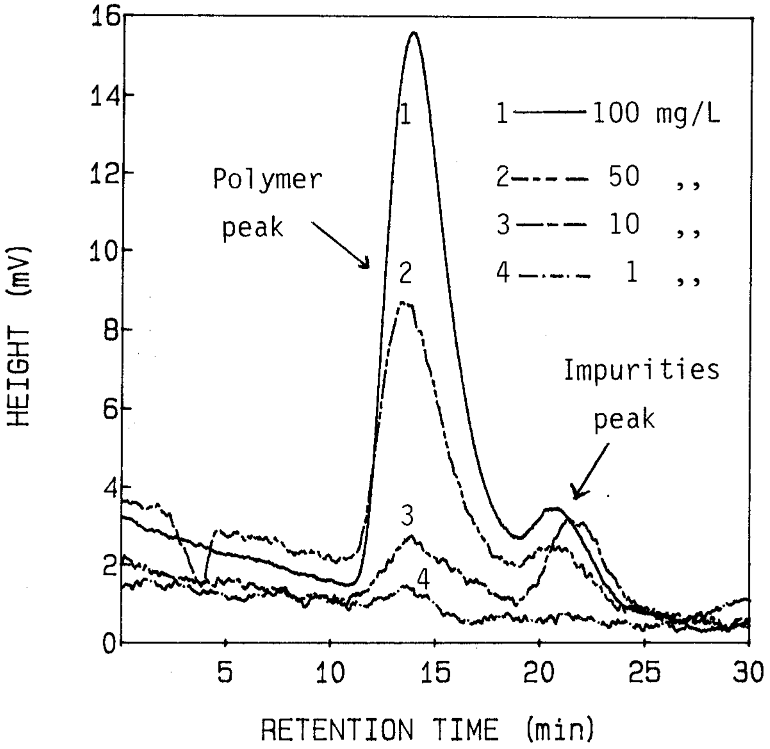


Figure 3 SEC of polymer A at various concentrations.

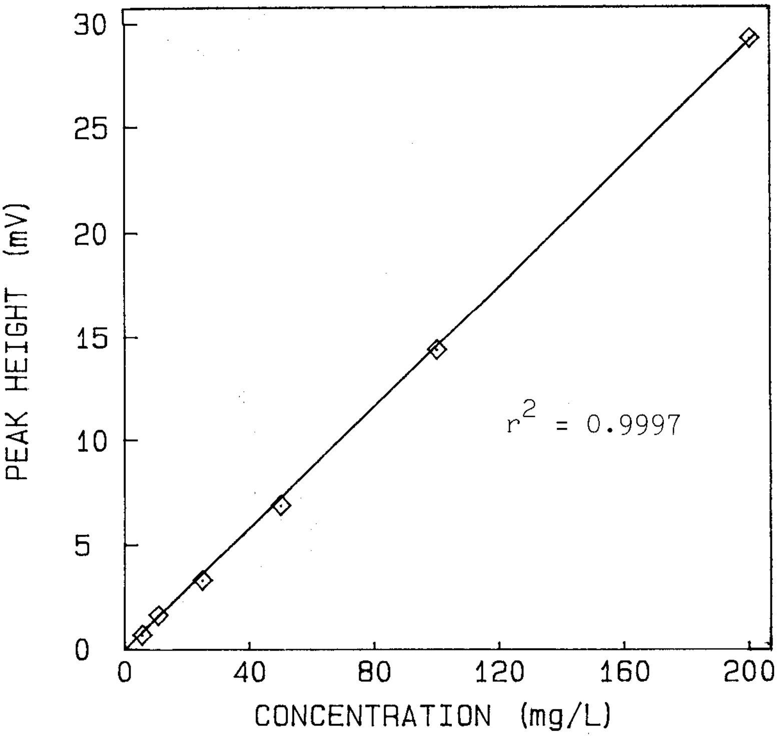


Figure 4 Standard calibration curve of polymer A.

A larger sample loop (1000 μL) was also used to improve the detection limit to 1 mg/L without affecting the separation efficiency, as shown in Figure 5. The salt concentration of the mobile phase was reduced to 0.01 M in accordance with the polymer/salt ratio shown in Figure 1, to prevent adsorption. Note that the minimum detection limit depends on the amount of acrylamide contained in the particular polymer. This minimum detection limit can also be lowered, provided only quantitative determination of polymer concentration is required, by using one column of small pore size packings (equal to or less than Catsec 1000) instead of two columns, as will be shown later in the analysis of an anionic polyelectrolyte.

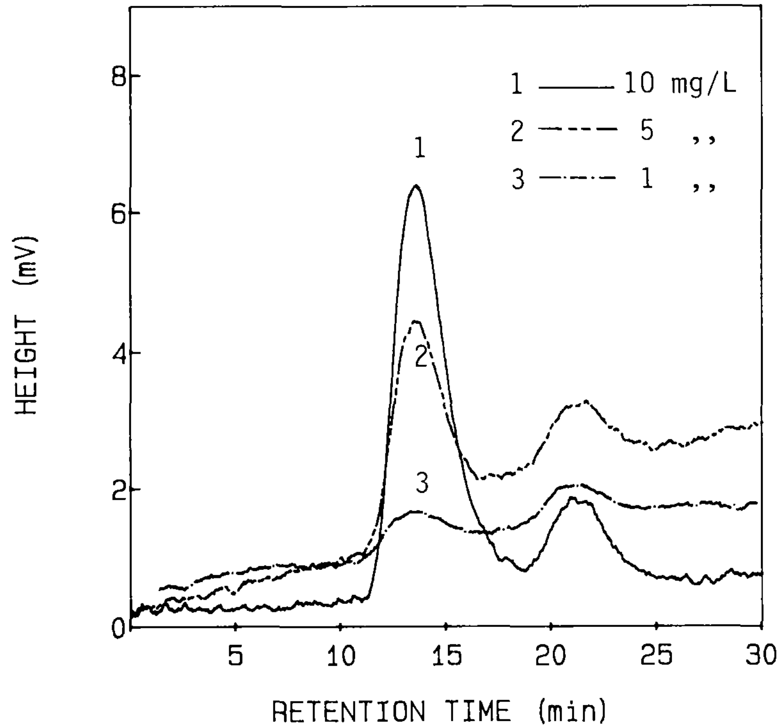


Figure 5 SEC of polymer A using a 1000 μL sample loop and 0.01 M KH_2PO_4 mobile phase.

Salt interference A sample of polymer A at 1 mg/L dissolved in 2.0 M NaCl was used to simulate the interference from salt and other small molecules. Interestingly, by using the expanded scanning mode in the Waters "Expert" software, the peak of polymer A at this low concentration could still be separated (and detected quantitatively) from the salt of very high concentration (Figure 6); such salt concentrations would usually interfere with most other methods mentioned previously. Therefore, SEC should be a useful tool for detecting trace amounts of polyelectrolytes in the presence of high salt concentration and other smaller molecule interferences, particularly colour and turbidity-causing compounds.

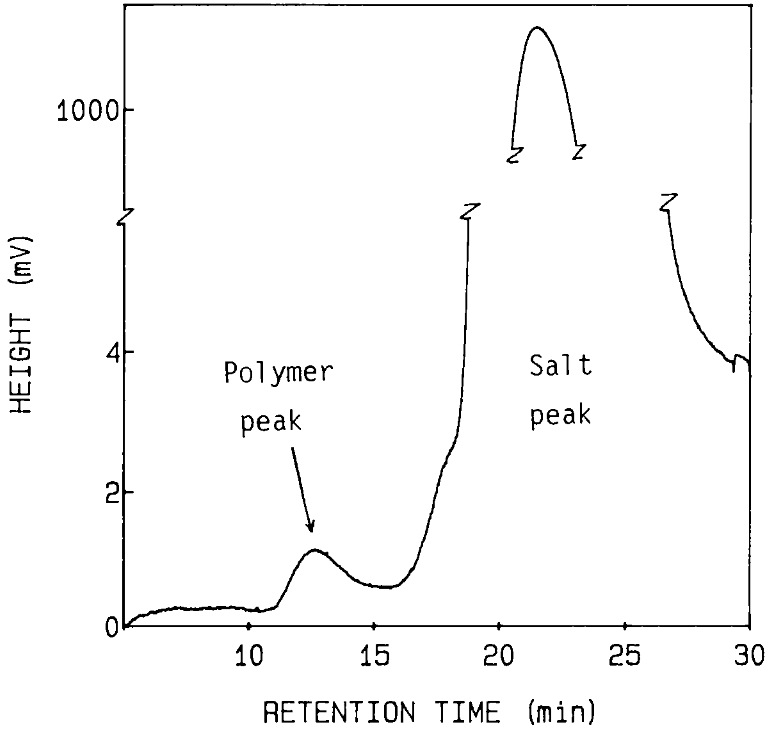


Figure 6 SEC of polymer A dissolved in 2.0 M NaCl using a 1000 μL sample loop and 0.01 M KH_2PO_4 mobile phase.

Polymer degradation study In those cases (e.g. degradation studies) where the molecular weight of a polymer has to be determined quantitatively, the columns must also be calibrated with polymers of known molecular weights and similar structure. Unfortunately, there were no suitable water-soluble polymer standards of very high molecular weight available. The columns were therefore calibrated with cationic polymers shown in Table I, their molecular weights having been determined as described previously. Figure 7 shows a selection of chromatograms used in constructing the calibration curve (Figure 8).

Figure 9 shows the use of SEC to study the degradation of polymer A by ozone, the latter being used in some municipal water treatment plants for disinfection. It can be clearly seen that the peak

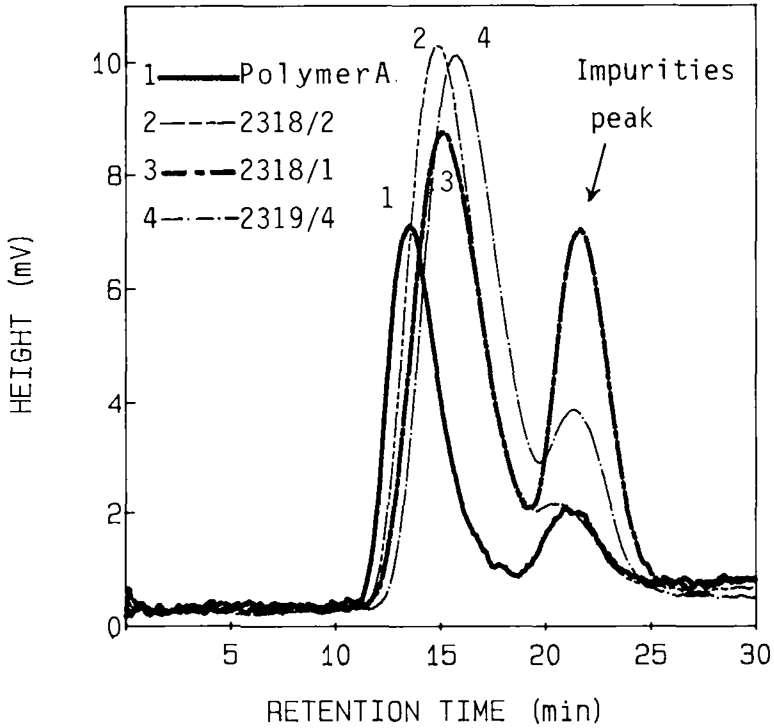


Figure 7 SEC of various cationic polyelectrolytes at 10mg/L.

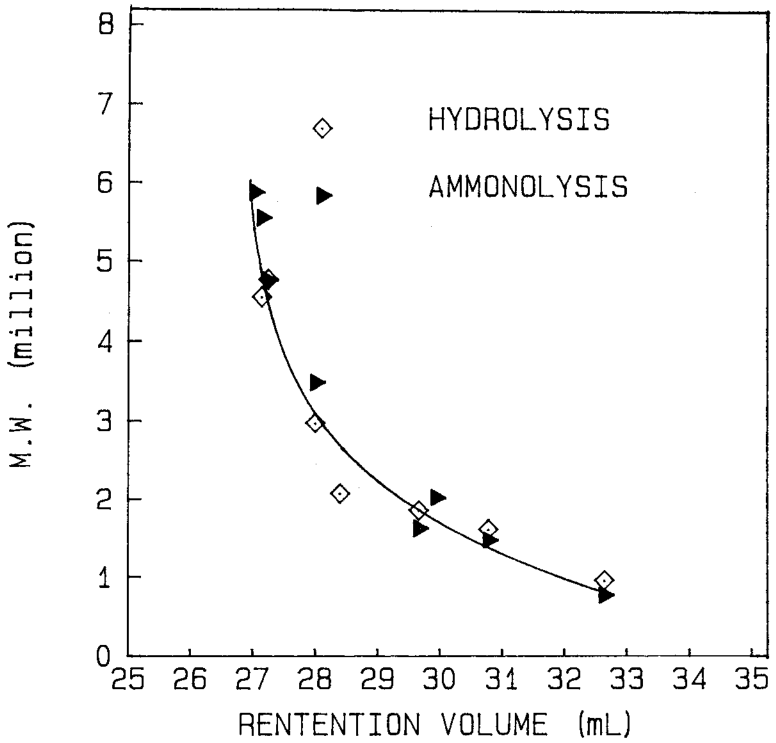


Figure 8 Molecular weight calibration curve for polymer A.

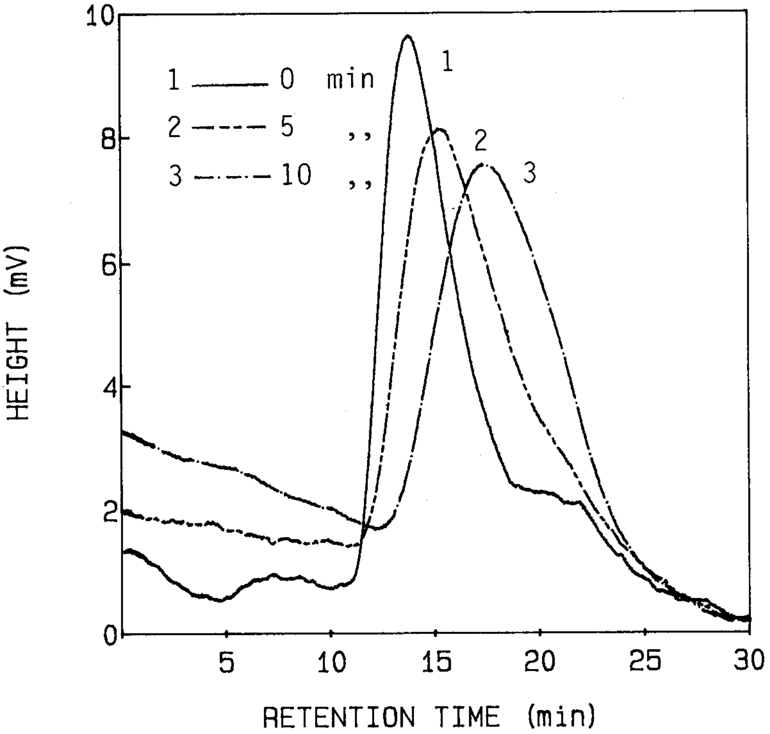


Figure 9 SEC of polymer A (100 mg/L) before and after ozonation (0.1 mg/L).

molecular weights of the ozonated polymers shifted to smaller values (i.e. longer retention time); this is in agreement with the results of Mallevialle[19], who reported similar work done on anionic polyelectrolyte. The molecular weight of polymer A decreased from about 6 million to less than 1 million after ozonation for 10 minutes according to the above calibration curve.

Analysis of anionic and nonionic acrylamide-based polyelectrolytes

Although this column packing has been recommended for cationic polyelectrolytes, it was also successfully applied to anionic partially hydrolysed polyacrylamide and non-ionic polyacrylamides (Figures 10 and 11).

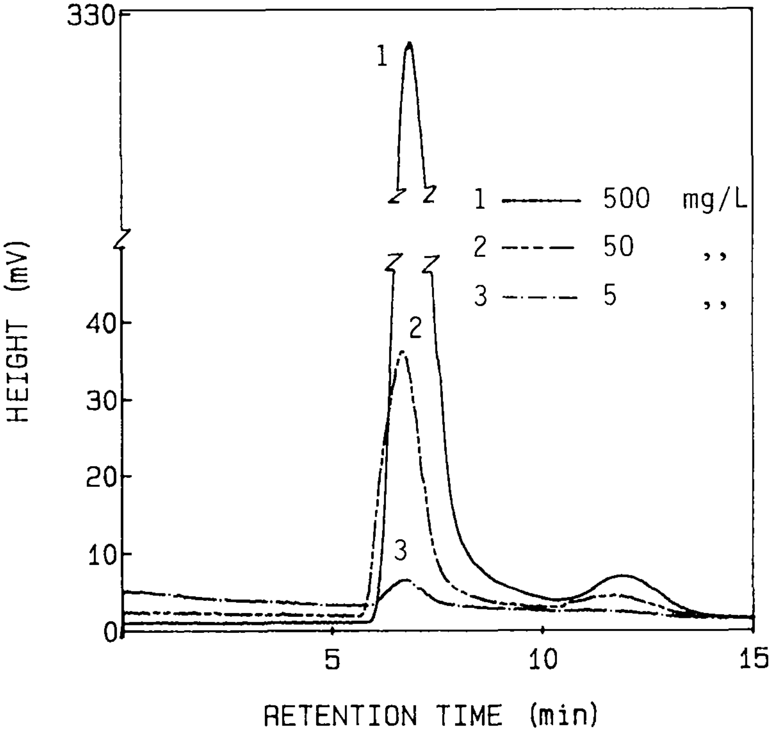


Figure 10 SEC of anionic polyelectrolyte at various concentrations on column 1000.

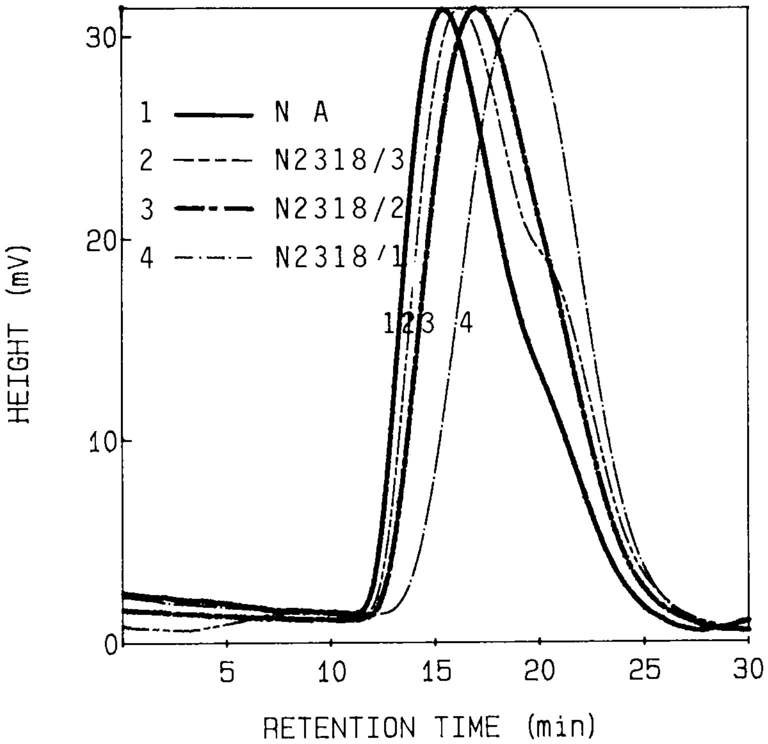


Figure 11 SEC of various non-ionic polyelectrolytes at about 200 mg/L.

Using an acidic mobile phase, the dissociation of the anionic part of the partially hydrolysed polyacrylamide is suppressed and becomes neutral, while the acrylamide part is protonated and becomes cationically charged. Therefore the partially hydrolysed polyacrylamide, like polyacrylamide itself, behaves as a cationic polyelectrolyte in the acidic mobile phase, and can be analysed by these columns.

CONCLUSIONS

It has been shown that SEC can be a powerful tool for quantitative and qualitative analysis of high molecular weight cationic polyelectrolytes, even in the presence of high salt concentrations which would interfere with most other methods. The column packing which is commercially available for cationic polyelectrolytes can also be successfully applied to non-ionic and anionic polyelectrolytes, provided an acidic mobile phase is used.

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