Size-Exclusion Chromatography of Cross-Linked Superabsorbent Polymers

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SYNOPSIS

Superabsorbent polymers are cross-linked poly(acrylic acid) with some degree of neutralization. These polymers have found extensive use as constituents in personal care products such as sanitary napkins, incontinent devices, and disposable baby diapers that absorb body fluids. Polymer networks are formed, which makes the chromatography of these materials impossible. In this study, hydrolysis under heat and high pH was used to break the cross-links, which allows for traditional size-exclusion chromatography to determine molecular weight and molecular weight distribution of the primary chains. For the chromatography, TSK-GEL®† PW_{XL} columns and TSK-GEL PW columns were used. The mobile phase was buffered with sodium chloride and sodium phosphate salts to eliminate ionic interactions. Detection was by refractive index. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

In the production and application of superabsorbent polymers, it is very important to know the molecular weight and molecular weight distribution of the polymer. These two properties can affect the quality and performance of a polymer. It is of the greatest importance to be able to determine the molecular weight distribution of a polymer, since even polymers with identical molecular weights and different molecular weight distributions can have different performances. Superabsorbent polymers are manufactured via the polymerization of partially neutralized acrylic acid using one of a variety of cross-linkers such as diethylene glycol diacrylate (DEGDA) or trimethylolpropanetriacrylate (TMPTA) that form ester-type cross-links. Also used as a cross-linker is ethylene glycol diglycidyl ether (EGDGE). The work presented here was done with polymers that have ester cross-links. Cross-linked superabsorbent polymers form networks of poly(acrylic acid) of infinite molecular weight that are impossible to directly analyze by chromatography. A method is presented that was successfully used to first break the ester cross-links and second to determine the relative molecular weight and molecular weight distribution of these cross-linked polymers. The analyses were performed using TSK-GEL PW_{XL}- and TSK-GEL PW-type columns[1,2] introduced by Toyo Soda in 1985. TSK-GEL column packings are hydrophilic, rigid, spherical, and porous polymeric beads that have excellent chemical and mechanical stability. Poly(acrylic acids) upon neutralization are polyelectrolytes that exhibit a number of properties based on their electrostatic nature in solution. The chromatography of water-soluble polymers and the solution properties of polyelectrolytes have been explored[3–13] by other researchers. The separation principle in size-exclusion chromatography is determined by the selective permeation of the polymers into and out of the mobile-phase-filled pores of the column packing. The elution of the polymer is then governed by the time that it expends in the pores. Hence, the larger molecules that expend less time in the pores elute first and the smaller molecules elute later. It is therefore accepted that the principal factor affecting the size-exclusion chromatography of a polymer is the hydrodynamic volume and not the molecular weight.

EXPERIMENTAL

Reagents

Poly(ethylene oxide) standards were obtained from Polymer Laboratories Inc. (Amherst, MA). Sodium chloride, sodium phosphate dibasic, and sodium azide were obtained from Fisher Scientific (Midland, MI).

Apparatus

The size-exclusion system consisted of two TSK columns GMPW$_{XL}$, TosoHaas (Montgomeryville, PA) part number 08025, and one TSK column G 1000 PW, TosoHaas part number 05760. TSKgel PW and TSKgel PW$_{XL}$ are hydrophilic, rigid, spherical, porous polymeric beads having a hydrophilic surface functionality of hydroxyl groups with excellent chemical and mechanical stability. TSKgel GMPW$_{XL}$ columns are packed with G 2500, G3000, and G6000 PW$_{XL}$ resins. The eluent used throughout this project was 0.3N NaCl with 0.03M Na$_2$HPO$_4$. The addition of salts is recommended by TosoHaas to eliminate non-size-exclusion effects. The size-exclusion behavior of polyelectrolytes is affected by the ionic groups attached to the polymer. It was reported[3] that chain expansions occur when an ionic polymer is dissolved because the electrical charges within the polymer coil generally exceeds that in the bulk solvent. It was also reported[4] that ion exchange and ion exclusion of polyelectrolytes are caused by the presence of dissociated silanol groups on silica-based packings, carboxylic groups on polymeric packings, or other ionized groups that have been introduced onto the packing. Cationic polyelectrolytes are adsorbed by ion exchange and anionic polyelectrolytes are excluded from entering the pores of the packing because of electrostatic repulsive forces. These effects can be, in many cases, eliminated by adding electrolyte to the mobile phase, which helps screen the electrostatic forces. The pH was maintained at 6.8 with 3% phosphoric acid. The solvent was filtered through a Micron Separations Inc. 0.1 μm nylon filter available from Fisher Scientific. Sodium azide, 400 ppm, was added to inhibit bacteria formation. The pump used was a Waters 590 with excellent flow reproducibility. The flow was kept at 1 mL/min. The detector was a Waters refractive index Model 410. The columns and detector cells were kept at 35°C. The injection volume was 200 μL. Samples were filtered through a 0.2 μm nylon Acrodisc®‡ 13 mm, available from Fisher Scientific.

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‡®Registered trademark of Gelman Sciences Inc.

Calibration with Poly(ethylene oxide) Standards

The apparent molecular weight of the samples was determined by comparison of the chromatographic behavior of the sample to that of standards with known molecular weights. Poly(ethylene oxide) narrow distribution standards ranging in molecular weight from 1470 to 1,390,000 were used for calibration. Figure 1 shows the calibration plot.

Correlation of Calibration with Narrow Molecular Weight Distribution Poly(acrylic acid)

Poly(acrylic acid) standards with a polydispersity of about 2, obtained from American Polymer Standard Corp. (Mentor, OH), were analyzed as samples to confirm the calibration obtained with poly(ethylene oxide) standards and to determine that the conditions of the analysis were appropriate. These standards had been characterized by American Polymers using a Brice-Phoenix light-scattering instrument at nine angles (30–130°) in 1.0M NaCl at a constant chemical potential, dialyzed against the reference solvent ($dn/dc = 0.179$).

Correlation of Calibration with Broad Molecular Weight Distribution Poly(acrylic acid)

A poly(acrylic acid) standard of broad molecular weight obtained from Polysciences Inc. (Warrington, PA) was characterized in our laboratory with a Chromatix KMX-6. This standard was also used to correlate the calibration with poly(ethylene oxide) standards.

Sample Preparation/Hydrolysis Conditions

The cross-linked polymer was added to 0.1N NaOH in water (1/100 ratio by weight) and placed in an oven at 75°C for 72 h to undergo hydrolysis. After

Polynomial Coefficients: Log(M) = A + BT + CT^2 + DT^3
A=1.52, B=1.33, C=-7.96e-2, D=1.18e-3
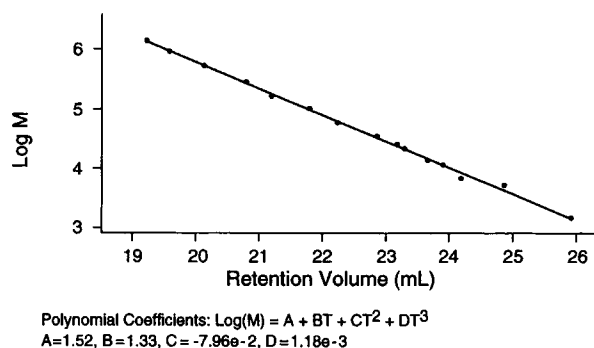
Figure 1   SEC calibration plot using poly(ethylene oxide) standards.

completion of the hydrolysis, the sample was diluted 1/10 with SEC eluent and injected into the system.

Quantitation

The software used for the calculations of molecular weight and molecular weight distribution was obtained from Polymer Laboratories Inc. (PL Caliber™ GPC/SEC software version 5.1). The computer was programmed to analyze the polymer peak. Any low molecular weight components were not included in the calculation.

RESULTS

Column Performance

The column resolution[3] was calculated following the formula

$$R_{sp} = \frac{0.58}{\sigma D_2}$$

The expression σD_2 is the product of the σ_R of ethylene glycol and the slope of the calibration curve of narrow fraction poly(ethylene oxide) standards. σ_R is equal to 0.5 times the width of ethylene glycol at 0.607 of the peak height. The R_{sp} for the system used during this study was 6.4. The theoretical plates/meter found using acetone were 24,000. Samples analyzed under the conditions listed in the Experimental section had a polydispersity between 4 and 6.
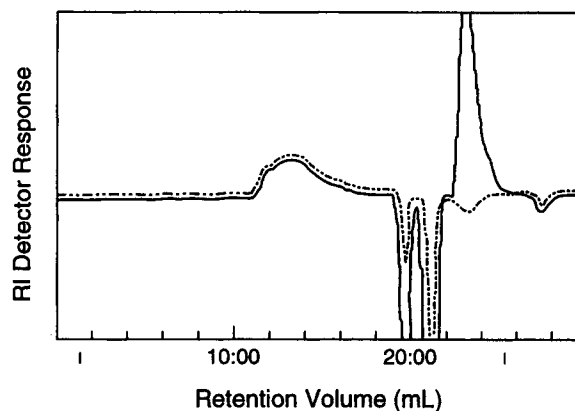
Precision Study

A 2-day precision study of a superabsorbent polymer of molecular weight of about 1.3×10^6 showed a relative standard deviation of $\pm 4.4\%$ at the 95% confidence level.

Table I Molecular Weight vs. Hydrolysis Time

Sample ID	M_w (10⁶)	Hydrolysis Time (h)
1A	2.99	72
2A	3.10	144
3A	3.00	216
1B	1.95	72
2B	2.10	144
3B	2.20	216

Samples 1 and 2 overlay of SEC Traces

Figure 2 Effect of hydrolysis on primary chain molecular weight. Overlay of sodium polyacrylate with no cross-linker, before and after hydrolysis. Solid line after hydrolysis; dashed line before hydrolysis.

Hydrolysis vs. Time

To demonstrate that the hydrolysis reaction was at equilibrium, two samples were analyzed after hydrolysis for 72, 144, and 216 h with the results shown in Table I.

Effect of Hydrolysis on Molecular Weight

A linear chain polymer with no cross-linker was submitted to the hydrolysis procedure. SEC characterization (Fig. 2) demonstrates that the cross-link hydrolysis conditions do not hydrolyze the polymer backbone.

Effect of Mass Injected into the System

The mass of sample injected into the system can have a deleterious effect on the chromatography. This is particularly true with high molecular weight polymers. The effect on the apparent molecular weight can be seen in Figure 3, in which a sample was injected at different concentrations. The graph in Figure 4 shows the effect of the polymer mass injected on the apparent weight-average molecular weight. As it was explained before,[3] "this type of column overloading appears to be due to a change in the effective dimensions (i.e., radius of gyration) of the macromolecular coils with concentration. . . ."[11] The apparent hydrodynamic volume of the solute decreased with increasing solute mass injected. A mass of around 20–100 μg can be safely injected.
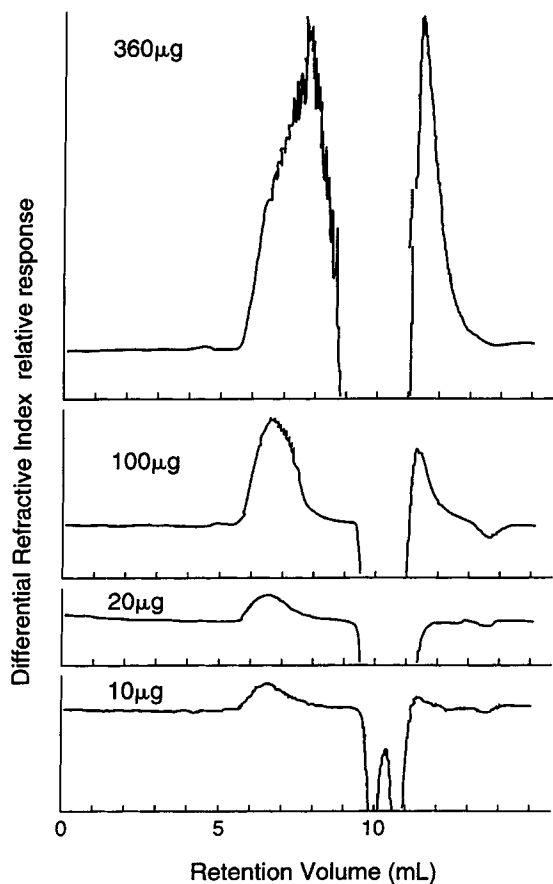
Figure 3   Effect of mass polymer injected on chromatographic behavior.

Relationship Between Extractables and Primary Chain Molecular Weight
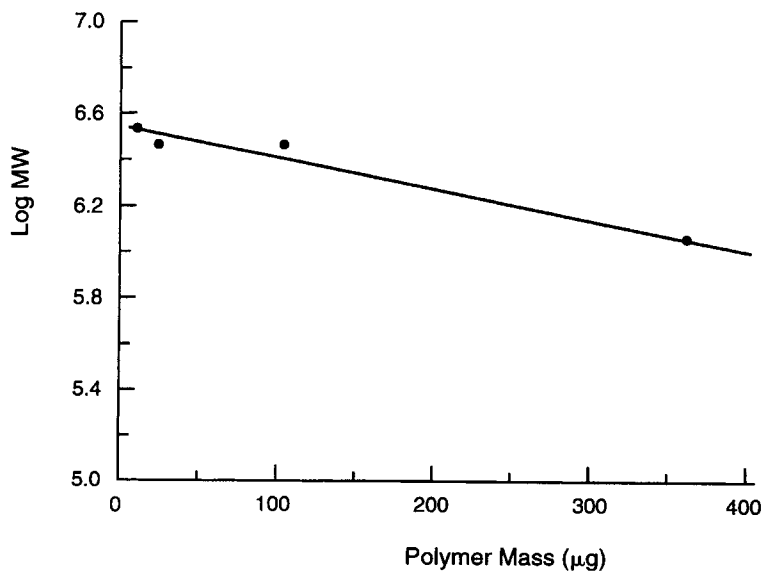
A linear relationship between the weight fraction of the extractable polymer and the mathematical product of the weight fraction cross-linker and the molecular weight of the primary polymer chains was obtained that is consistent with previous work.[14] These results are shown in Figure 5.

Effect of High Flow Rates

High flow rates can cause shear degradation with high molecular weight polymers.[15] It was suggested by Kim et al.[16] that poly(acrylic acid) has a high shear stability and what may look like degradation of the polymer by chain scission is actually due to a drastic coil deformation. A flow of 1 mL/min was found to be adequate for high molecular weight poly(acrylic acid).

CONCLUSIONS

The determination of molecular weight and molecular weight distribution of cross-linked superabsorbent polymers is possible after basic hydrolysis of the polymer to break the cross-links. It has been further demonstrated that a linear correlation exists between the weight fraction extractable polymer and the mathematical product of the weight fraction

Figure 4   Effect of mass polymer injected on apparent weight-average MW.
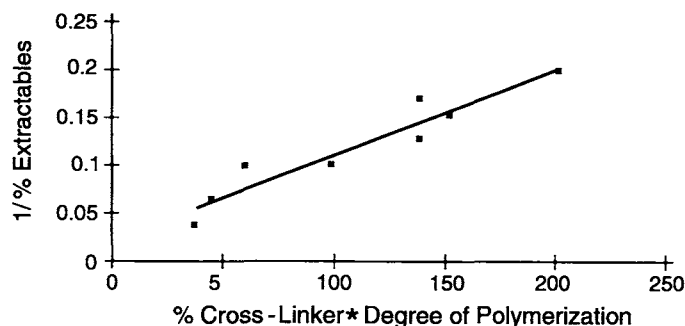
Figure 5   Relationship between extractables and the mathematical product of primary chain molecular weight and fraction cross-linker.

cross-linker and the molecular weight of the primary polymer chains.

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