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Evaluation of chemical structural heterogeneity of cationic acrylamide copolymers by high-performance liquid chromatography

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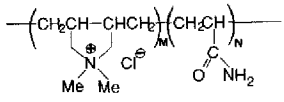
ABSTRACT

The chemical structural heterogeneities of two cationic acrylamide copolymers, methacryloxyethyl trimethylammonium chloride–acrylamide (AAM) and diallyldimethyl ammonium chloride–AAM, have been determined by high-performance liquid chromatography. In this method aqueous size-exclusion chromatography is combined with ion-exchange chromatography. Gradient elution with a sodium chloride solution is used. The resulting chromatogram shows the heterogeneity between polymer chains in solution. A comparison of the chromatograms of the original copolymer and its degradation product showed the heterogeneity along the copolymer chains.

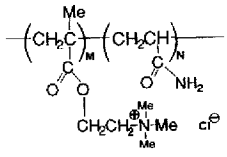
INTRODUCTION

Cationic acrylamide copolymers, such as diallyldimethylammonium chloride (DADMAC)–acrylamide(AAM) copolymer and methacryloxyethyl trimethylammonium chloride (MTMAC)–AAM copolymer, have been used extensively in paper manufacture and water treatment [1]. Differences in the performance of some copolymers with the same molecular weight and content of cationic groups have recently been found. Chemical structural heterogeneity of the copolymers may be one of the important factors in the performance.

DADMAC-AAM



MTMAC-AAM



Me = methyl

The by far most often used technique to elucidate the chemical structure of copolymers is ^{13}C NMR [2]. However, ^{13}C NMR is difficult to use for studying the chemical structure of cationic acrylamide copolymers. Firstly, the content of the cationic groups of this type of copolymers is normally very low, *i.e.*, less than 10 mol%, and the NMR signal of "effective" carbons becomes very low. Secondly, because this type of copolymer normally has a very high molecular weight (in millions), it is very difficult to prepare sample solutions of sufficiently high concentration for an increased NMR signal. Thirdly, also because of the high molecular weight of the polymer, the NMR peaks are usually broad.

The purpose of this paper is to introduce a new method for studying the chemical heterogeneity of cationic acrylamide copolymers by high-performance liquid chromatography (HPLC).

THEORY

Assume a polyelectrolyte chain having a homogeneous charge distribution. Charges are randomly distributed throughout the chain (Fig. 1). If this chain is degraded to several shorter chains, each resulting chain should also have a homogeneous charge distribution. On the other hand, if the original polyelectrolyte chain is heterogeneous, the degraded product will consist of some highly charged chains and some slightly charged chains.

HPLC has been used to fractionate copolymers according to their chemical composition [3]. The differences between the degradation products of homogeneous and heterogeneous polyelectrolytes should be readily distinguishable by HPLC. Assuming that the retention in HPLC is due to the number of cationic groups on the chains, the anticipated chromatograms of a polyelectrolyte and its degradation product will be as shown in Fig. 2. If the polyelectrolyte is homogeneous, the degradation product will consist of shorter, but homogeneous polyelectrolyte chains. The chromatogram of such product should show a single peak, eluted earlier than the original sample. If the polyelectrolyte is heterogeneous, the degradation product may contain polymer chains with a different number of charges, and even some uncharged polymers. Therefore, the HPLC may be multimodal and show very broad peaks.

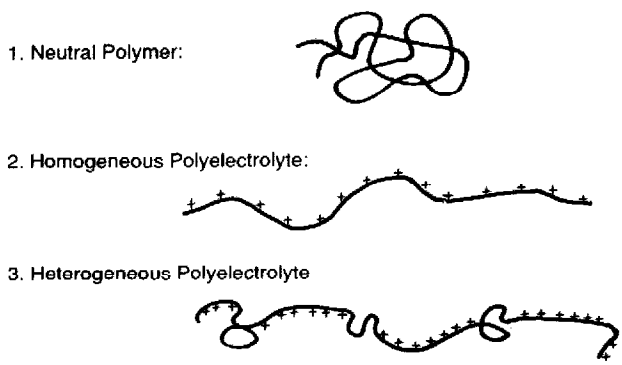


Fig. 1. Polymer chains in salt-free solution.

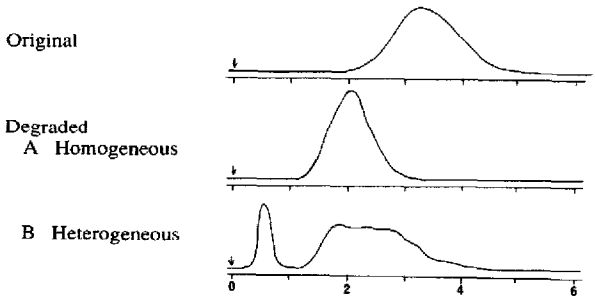


Fig. 2. Theoretical HPLC results of homogeneous and heterogeneous polyelectrolytes.

EXPERIMENTAL

The DADMAC–AAM and three MTMAC–AAM copolymers are experimental samples used at the Hercules Research Center, The DADMAC–AAM copolymer contains *ca.* 6 mol% of DADMAC. Three MTMAC–AAM copolymers contain about 5, 7.5 and 10 mol% of MTMAC, respectively.

The water used in the size-exclusion chromatography (SEC) and HPLC studies was purified with a Milli-Q reagent-grade water system (Millipore, Milford, MA, U.S.A.) and vacuum-filtered through a 0.2-μm nylon 66 membrane filter (Rainin 38-111) before chromatography. The GR crystal-grade sodium chloride was purchased from EM Chemicals (Gibbstown, N.J., U.S.A.).

A Bransonic 12 (Branson Ultrasonic, Danbary, CT, U.S.A.) ultrasonic cleaning bath was used to degrade the copolymers. SEC of polymers was performed with a Waters 510 (Milford, MA, U.S.A.) pump, which was equipped with a Rheodyne (Cotati, CA, U.S.A.) 7125 injector and a Waters 401 differential refractometer. Polymers were fractionated on a TSK PWH guard column and a PWXL mixed-bed column (both from Tosoh, Tokyo, Japan), in 0.24 *M* sodium formate aqueous solution (pH 3.7) as the mobile phase.

A Perkin-Elmer (Norwalk, CT, U.S.A.) Series 4 LC, equipped with a Rheodyne 7125 injector and a Schoeffel (Kratos, F.R.G.) 770 UV monitor were used in the HPLC analysis. Polymers were separated on a TSK PWH guard column, which was packed with cross-linked hydroxylated polyether gel having a low degree of residual carboxyl groups.

The infrared (IR) spectra were taken with a Perkin-Elmer Model 983 dispersive IR spectrometer. The samples were first dissolved in water, cast on germanium plate and then dried in a vacuum oven at room temperature.

RESULTS AND DISCUSSION

Molecular-weight reduction (degradation) of polyelectrolytes

High-molecular-weight polymer chains in solution can be degraded by ultrasonic vibration [4]. Fig. 3 shows the SEC curves of DADMAC–AAM copolymers at different ultrasonication times. The peak maximum of the original sample was at *ca.* 7.6 ml, which is the exclusion limit of this column set. When polymers were degraded

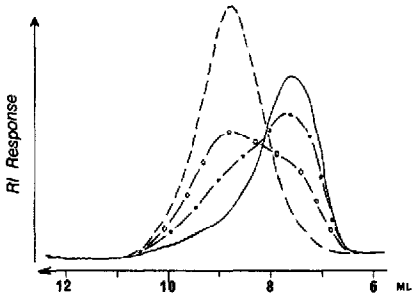


Fig. 3. Size-exclusion chromatography of a DADMAC–AAM copolymer and its degradation products after different ultrasonication times. Column: TSK PWH guard column (7.5 cm × 7.5 mm I.D., 13 μm particle size) plus TSK PWXL mixed-bed column (30 cm × 7.5 mm I.D.; 13 μm particle size); mobile phase: 0.24 *M* aqueous sodium formate (pH 3.7), 1.0 ml/min; detector: differential refractometer; ultrasonication equipment: Bransonic 12 ultrasonic cleaning bath. ——— = Original sample, ●—● = 0.5 h, ○—○ = 1.0 h, – – – = 3.0 h. RI = Refractive index.

by ultrasonic treatment, a new peak appeared at 8.8 ml, which corresponds to a molecular weight of $5 \cdot 10^5$, based on poly(ethylene oxide) calibration. After 3 h of ultrasonication, the high-moleular-weight peak almost completely disappeared. The polymer showed a narrow peak at 8.8 ml. The degradation of MTMAC–AAM copolymer by ultrasonic treatment also resulted in a narrow peak in SEC. These narrow molecular-weight distributions are very helpful for the interpretation of HPLC data.

HPLC

Many HPLC columns and different solvent gradient programs were tested for these low-charge-density, high-molecular-weight polyelectrolytes. The best choice from my experience was a TSK PWH guard column, which is packed with cross-linked hydroxylated polyether gel having a low degree of residual carboxyl groups. The solvent gradient program was from water to 0.2 *M* aqueous sodium chloride solution. Retention is probably based on an ion-exchange mechanism with some contribution of size-exclusion and reversed-phase partition chromatography. Since the concentration of negative charges (the residual carboxyl groups) on the gels is very low, the retention of multi-charge species, polyelectrolytes, is not as long as in normal ion-exchange chromatography. Because the retention of high polymers in liquid chromatography, except SEC, is strongly dependent on mobile phase composition, but not on column length [5], chromatography of this polymeric material does not require a long column. A short guard column was thus selected. This short SEC column also reduced the size-exclusion effect.

MTMAC–AAM

The chromatogram of a MTMAC–AAM copolymer under the above conditions is shown in Fig. 4. The sharp peak at 1.2 min was eluted by size-exclusion without other retention contribution. It should be due to high-molecular-weight polymer without, or almost without, positive charges. The second peak at 2.5 min is the peak of solvent impurity, such as acetone (introduced during polymer purification). Neutral polymers

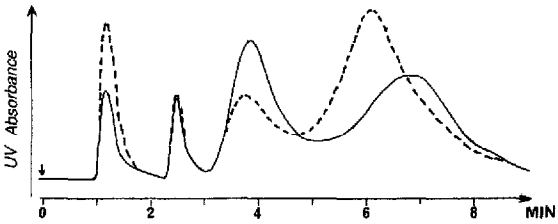


Fig. 4. Chromatograms of a MTMAC–AAM copolymer and its degradation product. Column: TSK PWH guard column (7.5 cm × 7.5 mm I.D., 13 μm particle size); mobile phase: linear gradient elution from water to 0.2 *M* aqueous sodium chloride in 10 min, 0.5 ml/min; detector: UV monitor at 230 nm; sample size: 50 μl of 0.2% solution. ——— = Original sample, – – – = degradation product.

will be eluted between these two peaks, depending on their molecular weight. After 2.5 min, the retention will be mainly due to ion exchange. Therefore, the longer the retention time, the more positive charges the polymer has. The chromatogram of the original sample in this figure (solid line) reveals two peaks in this area, which indicates that the sample probably contained two "types" of polyelectrolytes, one having much less positive charges and the other having much more positive charges. It should be mentioned that the high-molecular-weight (*ca.* one million or higher) polymers may be shear degraded during chromatography. Therefore, one should interpret the chromatogram with caution.

The dotted curve in Fig. 4 shows the chromatogram of the degraded sample. Since most of the degraded neutral polymers had a larger molecular size than the exclusion limit of this column, the peak at 1.2 min was still sharp. As this neutral polymer peak became larger, the less charged peak (3.7 min) became smaller and the highly charged peak (at *ca.* 6 min) shifted toward a shorter retention time. The peak at *ca.* 6 min is probably due to polymers with relatively homogeneous charge distribution or randomly distributed ionic groups. The polymer chains were degraded to shorter and still relatively homogeneous polyelectrolyte chains. The peak at *ca.* 3.7 min is probably due to the polymer with some ionic groups in one segment of the polymer chain and almost pure polyacrylamide in another segment of the chain side. Therefore, after degradation, this peak shifted only slightly. The intensity (corresponding to the polymer concentration) of this peak was reduced and that of the first peak (1.2 min) was increased.

The assignments of these peaks can be used to explain the chromatograms of different MTMAC–AAM copolymer samples shown in Fig. 5. The retention times of peaks a, b and c in Fig. 5A and B are about the same. However, the ratios of the peak sizes are different. Fig. 5A (the copolymer with 5 mol% of MTMAC) shows more neutral polymer (peak a) and less charged polyelectrolytes (peak b) than Fig. 5B (the copolymer with 7.5 mol% of MTMAC). It should be pointed out that the UV absorption of these peaks is due to a combination of amide and ester groups. Therefore, it is very difficult to calculate the composition of the polymers of the three peaks in each sample. On the other hand, Fig. 5C (10 mol% MTMAC) shows longer retention times of both peaks b and c than the corresponding peaks in Fig. 5A and B, which indicates that the 10 mol% copolymer sample has more ionic groups on both types of polyelectrolyte chains (peaks b and c).

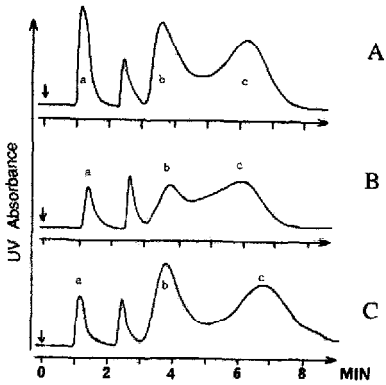


Fig. 5. Chromatograms of three MTMAC–AAM copolymers with different MTMAC content. Some chromatographic conditions as in Fig. 4. A = 5 mol% MTMAC; B = 7.5 mol% MTMAC and C = 10 mol% MTMAC.

Ultrasonic wave generates high temperature (*ca.* 2000 K) at micro-region in liquid phase [6]. Since the ester group of MTMAC is unstable at high temperature [7], there was concern that degradation by using ultrasonic treatment may induce hydrolysis of the ester to acid. The acid could then react with the adjacent amide group to form an imide [7]. The IR spectrum of an ultrasonically degraded MTMAC–AAM copolymer (Fig. 6) was compared with that of the original material. The two spectra were very similar except for a slight difference at 1720 cm^{-1}. Therefore, ultrasonication did not induce significant hydrolysis of the ester. Fig. 6 also shows the spectrum of a sample that was shear degraded by using a blender. This spectrum is essentially the same as that of the original sample. The chromatogram of ultrasonically

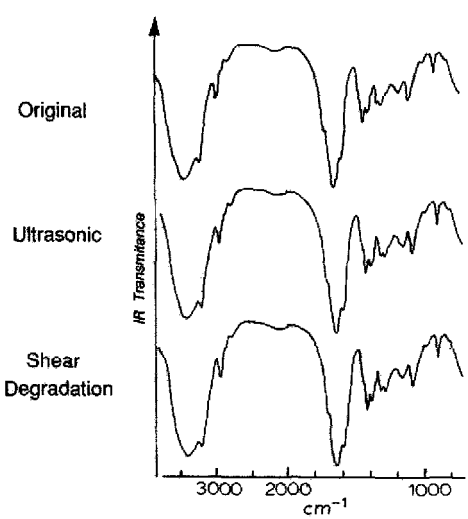


Fig. 6. Infrared spectra of an MTMAC–AAM copolymer and its degradation products. Samples were cast on germanium plates.

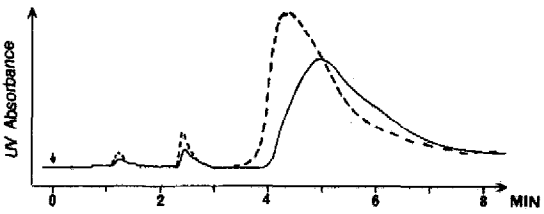


Fig. 7. Chromatograms of a DADMAC–AAM copolymer and its degradation products. Same chromatographic conditions as in Fig. 4. ——— = Original, – – – = degradation product.

degraded MTMAC–AAM copolymer was about the same as that of shear degraded product.

DADMAC–AAM copolymer

The chromatogram of DADMAC–AAM copolymer is much simpler. The original sample gave only one broad peak after 4.0 min (Fig. 7). There was almost no uncharged polymer. After degradation, the broad peak became narrower and was eluted earlier. These two chromatograms indicated that this DADMAC–AAM sample was chemically homogeneous. The broad HPLC peak of the original sample was probably due to a broad molecular weight distribution.

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