European Journal of Chemistry

View Journal Online
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Using free radical polymerization and Mannich reaction, synthesis and characterization of cationic polyacrylamides having similar molecular weight but different charge densities

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RESEARCH ARTICLE

10.5155/eurjchem.9.2.79-83.1684

Received: 28 January 2018
Received in revised form: 21 March 2018
Accepted: 04 April 2018
Published online: 30 June 2018
Printed: 30 June 2018

KEYWORDS
Synthesis
Charge density
Characterization
Mannich reaction
Cationic polyacrylamide
Free radical polymerization

ABSTRACT

Using free radical solution polymerization technique and Mannich reaction, five different polyacrylamides with similar molecular weight but variable charge densities were synthesized. High molecular weight polyacrylamides were synthesized using potassium persulfate and *N*,*N*,*N*',*N*'-tetramethylethylenediamine system as initiators. This was achieved by increasing the concentration of acrylamide monomer. They were then characterized by infrared spectroscopy, viscosity measurements and glass transition temperature measurement. These compounds with various cationic charge densities from 48.2, 161.7, 355, 425 and 485 C/g were prepared through Mannich reaction. The results indicate, by increasing the acidity of the polyacrylamide solution using sulfuric acid, the pH of the polyacrylamide solution decreases correspondingly. As a result, the positive charges increased resulting in the enrichment of charge densities.

Cite this: *Eur. J. Chem.* **2018**, *9(2)*, 79-83 **Journal website**: www.eurjchem.com

1. Introduction

Cationic polyelectrolytes namely cationic polyacrylamides are a group of polyelectrolytes that obtain their exclusive properties from the distribution and density of positive charges across the length of a macromolecular backbone and molecular weight. Cationic polyelectrolytes can efficiently interact with a suspension due to negatively charged particles, and oil droplets in the bulk phase. They are used in paper-making and treating wastewater. There is a greater variety of molecular structures in the cationic family than any of the other polyelectrolytes [1,2]. Synthetic cationic polyelectrolytes are polymers produced from raw materials of fossil fuels, by incorporation of cationic charges along the length of the chain that makes the polymer to be hydrophilic [3].

Cationic polyacrylamide is produced (which is utilized as a flocculant) by the interaction with dimethylamine and formaldehyde and then by quaternization. Furthermore, to obtain the weakly basic material, which is used in the conditioning of the sludge, changes in the scheme comprising the addition of dimethylamine and *m*-phenylenediamine are required [3].

There are many charge densities naturally occurring polyelectrolytes such as chitosan. Partially deacetylated chitin is a copolymer with 1:4 ratio of α-D-glucosamine and *N*-acetyl-α-D-glucosamine, which has inherent cationic properties or can be modified to yield a cationic polyelectrolyte. The most prominent of these is chitosan, a partially deacetylated chitin that can be considered as a 1:4 random copolymer of the commercial product. It is of medium molecular weight; has a charge density, which is pH dependent; and can be as high as 80%. The main applications of chitosan are in water purification, decolorizing dye house effluent, the treatment of food processing wastes, metal ion removal and sludge conditioning. A mixture of chitosan and bentonite has been tested for the removal of turbidity and color from surface waters, and found to perform as well as or better than alum or alum plus a cationic or non-ionic polyacrylamide, albeit at slightly higher cost [4].

The reaction of tannin with formaldehyde and amino-ethanol produces a weakly basic polyelectrolyte, which is more effective than alum in removing turbidity and especially color from river water [5].

ISSN 2153-2249 (Print) / ISSN 2153-2257 (Online)
http://dx.doi.org/10.5155/eurjchem.9.2.79-83.1684

Most commercial products are based on homopolymerization or copolymerization of acrylamide monomers. Acrylamide is often homopolymerized to form polyacrylamide, anionic polyelectrolyte [6]. Acrylamide is copolymerized with acrylic acid or sodium acrylate to make anionic polyelectrolyte [7]. Alternatively, anionic polyelectrolyte can be made via the homopolymerization of acrylamide and hydrolysis of some of the acrylamide groups to sodium acrylate [7].

Cationic polyelectrolytes are commonly made by copolymerization of acrylamide, with a suitable cationic monomer, such as dimethylaminoethyl acrylate or methacrylate [8]. Charge density depends on the number of ionisable groups and the degree of ionization. The number of ionisable groups is determined during polyelectrolyte synthesis e.g., the degree of hydrolysis of polyacrylamide or the proportion of cationic monomer incorporated. The degree of ionization depends on the nature of the ionic groups and the solution conditions. The cationic charge of the unquaternized or partially quaternized polyamines is pH dependent. Quaternary polyamine is very slightly affected by pH, remaining positively charged over a broad pH range. Some studies have shown that the interacttions of polyelectrolyte with metal ions in aqueous solutions were found to be pH dependent, ionic strength in addition to the ratios of both metal ions and polyelectrolyte [9].

Synthetic polyelectrolytes are currently the most used ones in the industry due to the following advantages: Structuration according to specific requirements, greater purity, higher quality stability, and greater efficiency compared to natural ones. They do not add insoluble substances to the sludge, nor do they modify the physical-chemical properties of the water, and therefore, liquids may be recycled. The main action of these products is to bring together and agglutinate the flocs formed by the coagulant; thus obtaining a considerable increase in the size of the same; and a subsequent increase in the settling rate speed, as well as an improvement in the quality of the effluent [10].

Mannich reaction was utilized for varied organic synthesis apart from polyelectrolyte synthesis, one such application used for β-aminoketones synthesis from cyclohexanone compounds to assess the mutagenic and antimutagenic potential of synthesized β-aminoketones using bacteria [11,12]. The synthetic β-aminoketones, which is a Mannich base derivative produced in the reaction of an amine, an aldehyde (formaldehyde), and a carbon acid, have a great potential to be industrial candidates for medicinal applications [13]. Mannich bases are achieved by reacting the amide group with formaldehyde and a secondary amine, to generate cationic derivatives. The derivative positively charged tertiary amine was produced in aqueous solution at moderate temperature and acidic condition. Subsequent reaction with dimethyl sulfate can be used to produce quaternary ammonium derivatives [3].

The present study involves the preparation and characterization of different charge densities polyacrylamides using Mannich reaction and free radical polymerization.

2. Experimental

2.1. Materials and reagents

Acrylamide (99%), *N*,*N*,*N*',*N*'-tetramethylethylenediamine (TMEDA) (98%), and potassium persulfate (98%) were purchased from Fluka, Germany, as laboratory grade. Dimethylamine and Formaldehyde were purchased from Merck, Germany, as laboratory grade. Sulfuric acid, nitric acid, propan-2-ol, acetone and methanol were purchased from Merck, Germany. A quaternary ammonium type in Cl^- form (Duolite 113), anionic exchange resin, and of 14-52 mesh particle size were purchased from BDH, Germany. Silver nitrate was purchased from R & M Chemical Co. UK.

2.2. Instrumentation and equipment

Memmert water bath was used for the polymerization reaction. A one-liter five-necked Pyrex glass reactor was placed into the water bath. The reactor was set with an automatic stirrer, condenser set with water collector, nitrogen gas inlet tube and thermometer.

2.3. Recrystallization of chemicals

A saturated solution was made by dissolving acrylamide (AM) in acetone at 56 °C. The solution was then filtered to eliminate unsolvable particles, and allowed to cool to get the crystallized material. The solid crystals were removed from acetone by filtration under suction using a Büchner funnel, washed with cold acetone and then dried out in vacuum at 60 °C for 24 h. This method was repeated twice. Distilled water was used for recrystallization of potassium persulfate at 100 °C using the same procedure described above. All other chemicals were used without purification.

2.4. Preparation of high molecular weight polyacrylamide

Acrylamide monomer is crystalline. It is relatively stable and is water-soluble and it is soluble in several organic solvents. Acrylamide polymerizes easily by free radical polymerization methods.

High purity of the monomer & initiators, and the absence of oxygen are essential in the polymerization process. High concentration of monomers and low concentration of initiators are required to synthesize high molecular weight polyacrylamide.

High molecular weight polyacrylamide was synthesized using the potassium persulfate and *N*,*N*,*N*',*N*'-tetramethylethylenediamine system as initiator. Later, under nitrogen atmosphere 30 g of acrylamide monomer were polymerized in 500 mL distilled water as a solvent, along with the (0.135 g) potassium persulfate (180 µL) TEMDA system as initiator to produce polyacrylamide with a high molecular mass. The mixture were placed in 500 mL five-necked Pyrex glass reactor equipped with a reflux condenser and mechanical stirrer, located in a constant temperature bath at 40 °C. Polymerization process was performed for 2 hours under stirring. The polyacrylamide was isolated and re-precipitated by pouring its solution into acetone. It was then dried under vacuum at 60 °C for 24 h.

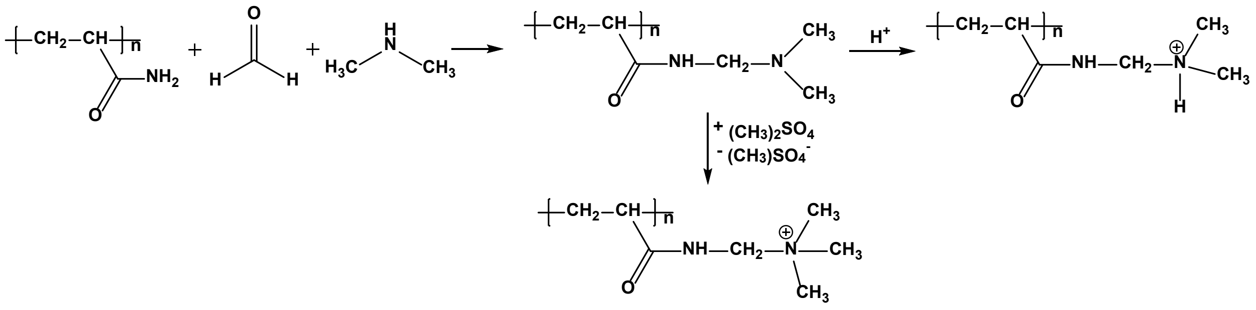
2.5. Characterization of synthesized polyacrylamide

2.5.1. Fourier transform infrared (FT-IR) spectra analysis

FT-IR technique is normally used in the investigation of polymer structure and analysis of their functional groups. Identification of acrylamide monomer samples and synthesized polyacrylamide were conducted. In general, 10 scans were applied for the prepared samples.

2.5.2. Glass transition temperature (T_g) measurement

Glass transition temperature (T_g) is an important characteristic property of a polymeric material, because its fabrication and/or applications depend on it. It is a feature of polymeric materials that they can be entirely amorphous, partly amorphous and partly crystalline. The glass transition temperature of the produced polyacrylamide was determined by Perkin-Elmer's Differential Scanning Calorimetry (DSC). It is equipped with a DSC cell set at 10 °C/min heating rate; the range of measuring temperature was between 25 and 250 °C.



Scheme 1

Samples between 5.0 to 10.0 mg of dry polyacrylamide were prepared into an aluminum pan for DSC measurement and then sealed with an aluminum cap. Similarly, an empty aluminum pan was used as reference.

2.5.3. Viscosity average molecular mass of polyacrylamide

The viscosity average molecular mass of polyacrylamides was carried out using the intrinsic viscosities of the polyacrylamides using Ubbelohde viscometer. The polyacrylamide solution was dissolved in distilled water. The calculations of polyacrylamides intrinsic viscosity were prepared after filtration using a sieve with 250 micron to eliminate any polyacrylamide gel lumps.

Dilute solution viscosity method was used to determine the viscosity average molecular weight of the polyacrylamide samples by determining their intrinsic viscosities. A test sample was made by dissolving 0.5 g of polyacrylamide in 100 mL distilled water at room temperature using magnetic stirrer. The resultant solution was filtered using a sieve with 250 micron to eliminate any polyacrylamide gel lumps.

Approximate amounts of the solution were transferred into Ubbelohde viscometer and the viscometer placed inside a water bath set at 25±0.1 °C and allowed to equilibrate. The efflux time i.e. the time taken for the liquid inside the viscometer to pass from the upper meniscus to the lower meniscus was determined. An average of the three readings which did not differ by more than 3 seconds was taken for each sample.

2.6. Preparation of cationic polyacrylamides using Mannich reaction

Positively charged (cationic) derivatives are obtained by modified method of reacting the amide group with formaldehyde and a secondary amine, to produce so-called Mannich bases. Reactions are carried out in aqueous solution at moderate temperatures and the derivative is a tertiary amine, which is positively charged only under acid pH conditions. Quaternary ammonium derivatives can be obtained by subsequent reaction with dimethyl sulfate as shown reaction in Scheme 1 [3]. Polyacrylamide solution was prepared by dissolving 10 g of polyacrylamide powder in 400 mL distilled water followed by sieving using a 250 micron sieve to eliminate undissolved solid lump. The resultant solution placed in a water-bath adjusted at 30 °C equipped with a mechanical stirrer for mixing. Aqueous solution of HCHO (21 mL, 37%) was added drop wise over a period of 30 min to the polyacrylamide solution at pH = 5 at slow mixing. After 15 minutes at this temperature, 63 mL of a 40% aqueous solution of $(CH_3)_2NH$ was added drop wise while maintaining the temperature ≤ 48-50 °C, to give a product of active cationic modification. Sulfuric acid was added to the solution above to adjust the pH to 10.5, 9.7, 8.3, 5.8 and 1.7.

2.7. Determination of the cationic content of the polyacrylamide

Common interfering organic ions, present in the polymer sample, were removed by extraction with propan-2-ol. About 5 g of the polymer was taken and mixed for 10 min with 50 mL of propan-2-ol. Once the granules had settled, the solvent was decanted and the process repeated. The final separation of the polymer from the solvent was achieved by filtration through filter paper. The polymer and the filter paper were placed in an oven maintained at 80 °C to evaporate the solvent.

Once dried, approximately 1.2 g of the granules were taken and placed into a 300 mL conical flask containing 5 mL methanol to wet and assist in the dispersion of the polymer. The deionized water (100 mL) was added to the mixture and the flask shaken to disperse the granules. The polymer solution was shaken on a laboratory flask shaker for two hours after which the solution was diluted to 200 mL, shaken, and passes through a sieve with 250 micron to eliminate polyacrylamide gel lumps.

A quaternary ammonium type in Cl^- form (Duolite 113), was used as anionic exchange resin and of 14-52 mesh particle size. The resin was supported in a 1.5 cm internal diameter glass tube and occupied a height of 6 cm. A glass wool plug prevented the resin passing through with the eluant.

The column was slurried with deionized water to eliminate air from between the particles and then washed through with 50 mL to remove excess chloride ions. The washing was continued until no free chloride ions were detected in the eluant. The detection of chloride ions was carried out by acidifying eluant samples with dilute HNO_3 and adding $AgNO_3$ solution to identify the presence of an AgCl precipitate. Once a clear eluant was obtained, the water level in the glass tube was dropped to a position 1 cm above the resin column to minimize dilution of the polymer solution.

The polymer solution filtrate was placed in the reservoir above the ion exchange resin and the connecting valve was opened. The air below the reservoir was evacuated by pumping the connecting rubber tubing. The Hoffman clip controller was opened to allow an approximate flow of 5 mL solution per min. When elution has completed, the solution was thoroughly stirred and approximately 10 g samples taken and accurately weighed into clean dry evaporating dishes to determine the dry weight. The estimation of dry weight was carried out in duplicate.

About 100 g of the remaining sample was accurately weighed into the titrating vessel and titrated against 0.1 M $AgNO_3$ solution, for chloride analysis, after acidification with a few drops of bench nitric acid. Chloride ion selective electrode was used to titrate for Cl^- ions.

2.8. Calculation

The results can be expressed as the charge amount in [Coulomb/g] or [micro-equivalent/g]. Therefore,

$$\text{The charge amount, } Q = \frac{V \times c \times F}{m} \quad (1)$$

where, Q = total charge amount [C/g] or [μeq./g]; V = Consumption [L]; c = Titrant concentration [mol/L]; m = Active substance of sample [g] and F = Faraday's constant 96485 [C/mol]. Since 500 micro-equivalent is equal to 100% cationic character [14], then the cationic character of the polyelectrolytes can be calculated.

3. Results and discussion

3.1. Synthesis of high molecular weight polyacrylamide

The free radical polymerization reaction produced the aimed polyacrylamide with high-molecular mass. Several techniques can be used to vary the molecular mass of polyacrylamide such as monomer concentration, initiator concentration and initiator type and polymerization temperature. The monomer concentration can be increased to 50% or more for high molecular weight polyacrylamide since the viscous polymer molecular weight is the internal phase. High purity of the monomer and initiators and the absence of oxygen are essential in the polymerization process.

Potassium persulfate/TMEDA system as initiator was used for the synthesis of high molecular weight polyacrylamide. TMEDA exerts a high promoting effect on the free radical polymerization, initiated by potassium persulfate. The presence of TMEDA increases the rate of polymerization by about three times. Potassium persulfate/TMEDA system can reduce the reaction time and react at moderate temperature (40 °C).

Potassium persulfate/TMEDA system was found to be an acceptable redox initiator for the production of high molecular weight polyacrylamide at moderate temperature and a maximum yield of 90-95% was obtained without any unwanted side products. The resulting product was a high viscosity white color liquid. Polyacrylamide was precipitated from the solution using acetone and then dried under vacuum at 60 °C for 24 h.

3.2. Fourier transform infrared spectra analysis

Fourier Transform Infrared Spectroscopy of polyacrylamide showed strong absorption at wavenumber 1655 cm^{-1}, due to the presence of a primary amide band, which is used to distinguish true polyacrylamide from the alternative polymerrization product poly-β-alanine, which has instead a secondary amide band at 1555 cm^{-1} [15]. The N-H stretching vibration band appears at 3448 cm^{-1} of the NH_2 group. Further, the absence of C=C band, which usually appears at 1610 cm^{-1}, proved that the acrylamide monomer has been completely converted to polyacrylamide and no residue of monomer is present in the polymer [16,17]. Ghosh *et al.* studied the FT-IR spectra of polyacrylamide; their finding is in a good agreement with our results [18].

3.3. Glass transition temperature measurement

The glass transition is a physical change from the glassy to the liquid state, which occurs in amorphous solids when they are heated. Differential Scanning Calorimetry (DSC) is used to determine glass transition temperature. The DSC thermogram of high molecular weight polyacrylamide was determined. The glass transition temperature of high molecular weight polyacrylamide appeared at 148.73 °C. This shows that up to this high temperatures the polyacrylamide was in the glassy state and thus relatively resistant to the ingress (way in) or egress (way out) of small molecule penetrate, and it is necessary to use higher temperatures to put the polymer in the rubbery state where adsorbed solvent molecules are sufficiently mobile to be desorbed [16,17].

3.4. Determination of approximate molecular weight

Viscometry and application of Mark-Houwink equation is one of the simplest and most rapid methods used for determining the molecular weights of polymers. Molecular weight of the polyacrylamide samples can be estimated from the intrinsic viscosity values. Mark-Houwink equation is generally employed for the estimation of molecular weight of linear polymers. The molecular weight of polyacrylamide sample was determined by determining their intrinsic viscosities using Ubbelohde viscometer. Therefore, in this study, the concentration of polyacrylamide solutions ranging from 1×10^{-3} to 5×10^{-3} g/mL was prepared by appropriate dilution of the test sample with distilled water. By increasing the concentration of polyacrylamide, the intermolecular interactions increased leading to the formation of intermolecular complexes resulting in the enhancement of densities. As a result, relatively higher values in the efflux time at higher concentration of polyacrylamide solution were predictable. The values of relative, specific, reduced and inherent viscosities of the various concentrations of the high polyacrylamide were determined.

It was found that by increasing the polyacrylamide concentrations from 1×10^{-3} to 5×10^{-3} g/mL the efflux time increased. As a result, the relative viscosity increased with an increase in the polyacrylamide concentration. Other viscosities, namely specific and reduced viscosities, also increased with an increase in the polyacrylamide concent-ration. On the other hand, the inherent viscosity was inversely proportional to the increase in polyacrylamide concentration. The intrinsic viscosity [η], which is defined as the intercept on the abscissa at zero concentration, was determined by plotting the reduced viscosity of the solution of different concent-rations of polyacrylamide solutions. Intrinsic viscosity of the high polyacrylamide sample was obtained as shown in Figure 1.

3.5. Cationic polyacrylamides with different charge density using Mannich reaction

The Mannich reaction of polyacrylamide produced the aimed cationic polyacrylamide with different charge densities. Mannich reaction was carried out in aqueous solution at reasonable temperatures and the derived is a tertiary amine, which is positively charged only when acid is added to the Mannich base solution [3]. The charge density (cationic content) of the cationic polyacrylamide can be varied by adjusting the pH of the Mannich base. Sulfuric acid was added to the above Mannich base solution to adjust the pH to 10.5, 9.7, 8.3, 5.8 and 1.7 to produce the targeted very low, low, medium, high and very high-charge densities cationic polyacrylamide products respectively.

3.6. Determination of the cationic amount of the polyacrylamides

The charge densities of the cationic polyacrylamide samples were determined using conductometric titration method in which, the end-point of the cationic polyacrylamide samples was determined, using chloride ion selective electrode [19].

Table 1. The charge densities and % cationic nature of cationic polyacrylamides.

Polymer	Viscosity average molecular weight (g/mol)	Charge density (C/g)	% Cationic nature
A	1.5×10^6	48.2	9.6
B	1.5×10^6	162.0	32.4
C	1.5×10^6	355.0	71.2
D	1.5×10^6	425.0	85.0
E	1.5×10^6	485.0	97.0

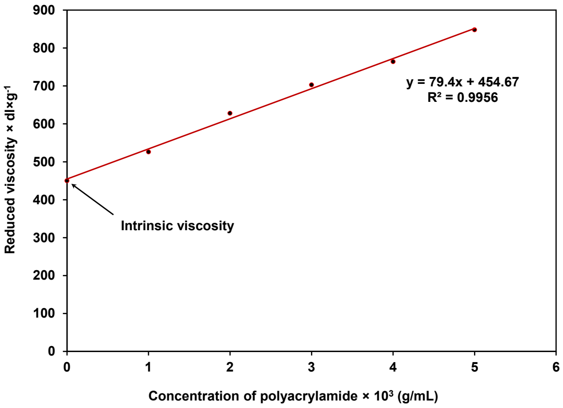


Figure 1. Determination of intrinsic viscosity of high molecular weight polyacrylamide.

The values of charge density of the cationic polyacrylamides were determined according to the equations given in calculation section. The amount of 0.1 M silver nitrate solution required (V = [L]) to reach the end-point was used to calculate the charge density (Q = [C/g] or [µeq/g]. The V value, which is defined as the consumption [L], was determined by plotting the amount of the 0.1 M silver nitrate versus the reading of chloride ion selective electrode (mV). The results of the end-point of the very low, low, medium, high and very high cationic polyacrylamide samples are calculated. The results of charge density and charge character (%) are tabulated in Table 1.

4. Conclusion

In the present investigation, five different polyacrylamides with similar molecular weight but variable charge densities were synthesized using Mannich reaction and free radical polymerization. It was found that by increasing the acidity of the polyacrylamide solution using sulfuric acid, the pH of the polyacrylamide solution decreases correspondingly. As a result, the positive charges increased resulting in the enrichment of charge densities. Therefore, relatively higher values in the amount of V at higher concentration of sulfuric acid were predictable.

Acknowledgements

The authors are highly grateful and thankful to the Research Center & Preparatory Health Sciences Department of Riyadh Elm University, Riyadh, Kingdom of Saudi Arabia for their valuable cooperation and infinite support.

Disclosure statement

Conflict of interests: The authors declare that they have no conflict of interest.
Author contributions: All authors contributed equally to this work.
Ethical approval: All ethical guidelines have been adhered.
Sample availability: Samples of the compounds are available from the author.

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