

Controlled conversion of polyacrylamide into polyacrylic acid

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Summary

Interaction of nitrous acid with aqua solution of poly(acrylamide) gives poly(acrylic acid) in quantitative conversion yields. The reaction proceeds smoothly, with simultaneous evolution of nitrogen, provided that the temperature below 5°C. The procedure presented provides a versatile route to prepare acrylic acid-acrylamide copolymers in any desired composition, by adjusting molar ratio of nitrous acid.

-Keywords: Poly(acrylamide), poly(acrylic acid co-acrylamide), poly(acrylic acid), nitrous acid reaction.

Introduction

Poly(acrylic acid) is one of the most important water-soluble polymers. It has found many applications in textile sizing, adhesives and coatings. Incorporation of a few percent of acrylic acid into a copolymer imparts a degree of hydrophylicity to the copolymer. Those copolymers gain adhesion capability. Also, presence of acrylic acid moieties in a copolymer provides post-crosslinking capabilities, by treating with appropriate difunctional reagents, such as diamines, diols and epoxides(1). Since poly(acrylic acid) has ionizable carboxyl groups in each repeating unit, it shows unusual solution behavior in polar solvents, which differs from those of non-ionic polymers. This behavior is termed as polyelectrolyte behavior.

There are two main routes to prepare poly(acrylic acid):

i) Polymerization of acrylic acid monomer and ii) acid or alkaline hydrolysis of suitable prepolymers, such as polyacrylic acid esters(2), poly(acrylonitrile)(3) and poly(acrylamide)(4)

Polymerization of acrylic acid monomer is fairly exothermic and may cause to severe explosions. For this reason only small quantities (up to 10 ml) of acrylic acid is recommended to homopolymerize. Another limitation is that, acrylic acid monomer itself shows storage and handling problems because of its spontaneous polymerization capability. It polymerizes thermally even in presence of inhibitors. Its storage in large containers is not safe and extreme care should be undertaken.

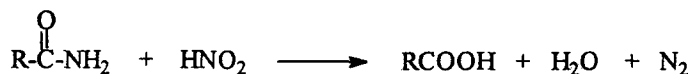
For preparing large quantities of poly(acrylic acid) hydrolysis of polyacrylic acid esters, poly(acrylamide) or poly(acrylonitrile) is often preferred. By partial hydrolysis of these polymers it is possible to obtain the corresponding copolymers. For instance, partial hydrolysis of poly(alkyl acrylates) gives acrylic acid-acrylic ester copolymers. Similarly acrylic acid-acrylamide copolymers can be prepared by partial hydrolysis of poly(acrylamide). Hydrolysis of poly(acrylonitrile) can give acrylic acid-acrylamide-acrylonitrile terpolymers.

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The extent of hydrolysis depends strongly on the reaction conditions followed. Depending on temperature, concentration and reaction time also some side reactions yielding crosslinked structures, may occur. For instance, during hydrolysis of poly (acrylamide) in concentrated solutions may result in crosslinking through imide linkages. Obviously it is difficult to control the extent of these hydrolysis.

In the present study we have described a facile method for the preparation of poly (acrylic acid) and acrylic acid-acrylamide copolymers by the reaction of nitrous acid with poly (acrylamide) in water.

Reaction of nitrous acid with primary amides is fast and results in formation of carboxylic acid and gaseous nitrogen.



In the study, we have observed that at the temperatures below 5°C conversion yields can be controlled stoichiometrically by adjusting molar ratios of nitrous acid and amide content of feeding solutions.

Experimental

A very high molecular weight ($M=23,000,000$) of poly (acrylamide) (Allied Chem.) NaNO_2 , HCl (Merck) and other analytical grade chemicals were used without further purification.

DSC thermograms were taken by Perkin Elmer DSC-6, with 10°C/min heating rate. Viscosity measurements were carried out in water solutions at $30 \pm 0.2^\circ\text{C}$ (in 0.1g /100 mL concentrations) by using Canon-Fenske viscometer.

Conversion of poly (acrylamide) into poly(acrylic acid) :

2 g. poly(acrylamide) is dissolved in 300 ml water in a 500 ml volume of flask. To this solution 2 g.(29.0 mmol) NaNO_2 is added and the mixture is stirred for 15 min to dissolve sodium nitrite. The reaction flask is transferred to an efficient fume cupboard and placed in an ice-bath. While stirring vigorously 5.8 ml of 5M. HCl solution (which is equivalent to the sodium nitrite) is added dropwise in about 20 min.

The mixture is stirred for 6h. at 0°C. The reaction is visually followed by nitrogen evolution. Stirring is continued for another 18 h. at room temperature. At the end of this time nitrogen evolution is almost completed. To remove trace amounts of nitroxide residues the mixture is heated to 40-50°C for about 5 min. After cooling, the reaction content is poured into 200 ml of ethanol. The polymer precipitated is filtered. Wet product is dispersed in 20 ml. acetone and the acetone is decanted. This operation is repeated five or six times and solid product is dried under vacuo for 72 h. at 40°C. The

yield 1.2 g. Elementary analysis of the product gives only 0.1 % N₂ content, which corresponds to 99.5% conversion. Obviously this is within experimental error limits.

Preparation of acrylic acid-acrylamide copolymers

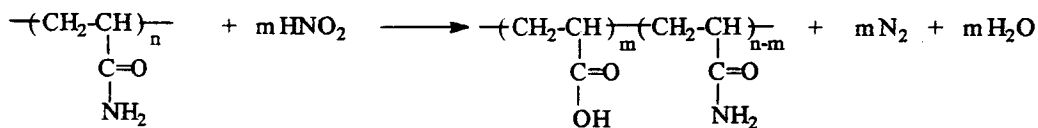
The same procedure was followed for the preparation of copolymers by changing the quantity of nitrous acid which was formed insitu, from equivalent amounts of NaNO₂ and HCl. A series of copolymers was prepared by using nitrous acid in different ratios. For this purpose, calculated amounts of NaNO₂ and HCl were used, so as to give copolymers with 10%,20%...carboxyl contents.

Determination of the carboxyl contents :

Carboxyl content was determined by conductometric titration of aqua solution of the copolymer samples. For this purpose 50 mg of each sample is dissolved in 50 ml of distilled water by stirring at room temperature, for 96 h. To the cooled solutions 10 ml. of 0.1 M NaOH solution is added and excess of NaOH is back titrated with 0.1 M HCl solution conductometrically (by using Siemens, WPA, CM35)

Results and Discussion :

Upon treating with nitrous acid amide groups in poly(acrylamide) can be totally or partially transformed into carboxyl groups. Since the reaction is quantitative, by this way it is possible to obtain poly (acrylic acid) or acrylic acid-acrylamide copolymers in any desired composition. Based on this, the following stoichiometric equation can be written.



The reaction can be followed visually by observing the nitrogen bubbles in solution. Also the extent of the reaction can be followed by gasometrical measurement of the nitrogen liberated. At the temperatures above 5°C nitrous acid tends to decompose into volatile nitroxides and these nitroxides may escape from the aqueous solution, without reacting. However in cold solutions the reaction proceeds smoothly.

In the study a series of copolymers were prepared by using different amounts of nitrous acid. Carboxyl contents of the resulting copolymers were determined by conductometric titration. Based on

the carboxyl contents, conversion yields were calculated and compared with the theoretical conversion yields deduced from the stoichiometric equation. Relevant data has been tabulated in Table 1.

Table 1: Characteristics of the Copolymers obtained.

Run	HNO ₂ ^(a) (mmol/g PAM)	T(%) ^(b)	P(%) ^(c)
0	-	0.0	0.0
1	1.4	10	10.04
2	2.8	20	21.32
3	4.2	30	31.22
4	5.6	40	39.73
5	7.0	50	51.10(48.8) ^d
6	8.4	60	61.09(60.9) ^e
7	9.8	70	72.53(69.8) ^d
8	14.0	100	100.0(99.95) ^e

(a) : Feeding composition

(b) : Theoretical conversion yield, which is equal to the molar ratio of nitrous acid to the amide content ($[\text{HNO}_2]/[\text{CONH}_2]$ (mol/mol))

(c) : Practical conversion yields based on the carboxyl contents.

(d) : Based on gasometric measurement of the nitrogen (evolved)

(e) : Based on nitrogen content by elementary microanalysis.

Table 1 represents that practical and theoretical conversion yields are almost equal. For some samples there are little differences between the practical and theoretical conversion yields due to unremoval water even after drying for extended time of periods. Also gasometric measurement of evolved nitrogen, a very time consuming process, can give the subsequent conversion yields. As shown in Table 1 these results are also in consistent with those obtained from the conductometric titrations. The conversion yields can be obtained more directly by monitoring the nitrogen contents by elementary micro analysis.

However this was not possible for the products with low conversions, due to formation of chary residues during the experiment. But the copolymers with high carboxyl contents gave satisfactory results.

Also IR spectra of poly(acrylamide), acrylic acid-acrylamide copolymer (1/1) and poly (acrylic acid) obtained by this method have been given in Fig.1 for comparison. IR spectra of the later two match well with those given in the literature (5). These evidences establish the proposed transformations qualitatively.

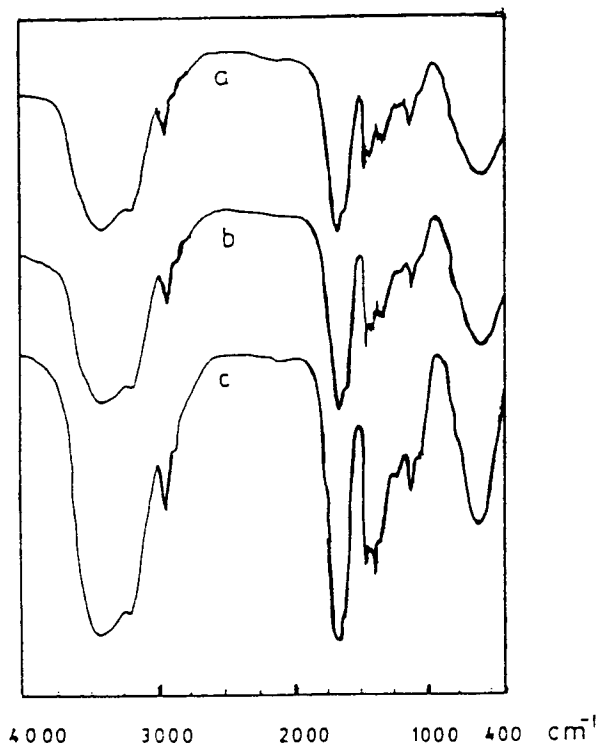


Fig.1 IR spectra of poly(acrylamide) (a), acrylic acid-acrylamide copolymer(1/1) (b) and poly(acrylic acid)(c).

It is important to note that, excess of nitrous acid is not recommended for the preparation of poly(acrylic acid). Because in that case surprisingly the resulting product contains nitrogen. Indeed, when we used two-fold excess of nitrous acid, the elementary microanalysis showed 1.9% nitrogen. This little nitrogen content can not be ascribed to the unreacted amide groups. Most probably this must be because of the formation of C-nitroso compounds through the main chain carbon atom carrying carboxyl group. Because nitrous acid is known to react with activated methylene groups to form oximes as in case for the reaction of acetone with nitrous acid yielding acetone oxime. Whereas methylene groups possessing one hydrogen atom give C-nitroso compounds.

In our case, the most activated methylene group in poly(acrylic acid) is the one carrying carboxyl group. Having one hydrogen atom this methylene group can give C-nitroso compounds.

On the other hand, the inherent viscosities of the copolymers obtained by this method do not change linearly with their compositions. Obviously this is because of the polyelectrolyte of acrylic acid segments in the copolymers.

On conclusion, the method described here offers a facile method to prepare acrylic acid-acrylamide copolymers, starting from poly(acrylamide). The extent of the reaction can be controlled stoichiometrically by adjusting molar ratios of the reaction components.

References

1. R.S. Stein, S. Krimm and A.V. Tobolsky, *Textile Res.J.*19(1),8(1949).
2. A. Katchalsky (Katzir) and H. Eisenberg. *Polym.Sci.*6,145(1951).
3. R.L. Morgan (to American Cyanamid Co.,) U.S. Pat.2,775,557(1956).
4. G. Smets, *Makromol.Chem.*34,190-205(1959).
5. D. O. Hummel and F. School, *Atlas of Polymer and Plastic Analysis*, Verlag Chemie Weinheim, New York (1978).