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Polyacrylamides with Coloured Groups for Trace Analysis in Water

Philippe Gramain and Philippe Myard

Centre de Recherches sur les Macromolécules, CNRS,
6, rue Boussingault, 67083 Strasbourg Cédex, France

SUMMARY

The polymerization of acrylamide in presence of some coloured monomers was investigated in order to study a spectroscopic method of titration of very diluted solution of polyacrylamide in water. Best results have been obtained with the N,2,4 dinitroacryline-acrylamide monomer incorporated in low content (1/3000 mole). The presence of such low quantity of dyes does not affect the polymerization and the hydrolysis of the obtained copolymers leaves intact the dye groups. By using different dyes with different spectroscopic behaviour, this method can be very usefull to solve problems of mixture and molecular weight or hydrolysis polydispersity of polyacrylamides.

INTRODUCTION

The increasing use of polyacrylamide as flocculating, gelling or stabilizing agents has created considerable interest in the determination of these materials in water. In particular when studying the adsorption properties of these polymers it is necessary to use a method of analysis able to detect minute quantities. In addition, it is to be desired that the method is as simpler, more precise and more selective as possible. Two main methods have been proposed using a turbidimetric (GRIOT and KITCHENER, 1965) or a nitrogen content (NEDELCHEVA and STOILKHOV, 1977) determinations. However in many cases these methods are not enough sensitive, rapid and selective. For the purpose of a study of the adsorption of polyacrylamides in porous media (MYARD and GRAMAIN, 1981) we used a colorimetric method based on the spectroscopic properties of polyacrylamides containing a very few percentage of coloured units. In addition of its high sensitivity, easiness and rapidity, this method is very interesting for analysing problems involving mixed or polydispersed systems. Various coloured monomers with different optical properties can be incorporated and this makes possible the distinction between polyacrylamides of different molecular weights or different degrees of hydrolysis. It the number of coloured comonomers which is possible to incorporate is very large, it is however necessary to consider some

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restrictive conditions.

- a coloured monomer with a molar absorption coefficient (ε) as high as possible has to be choosen

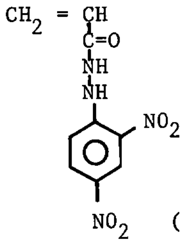
- the comonomer must be as water-soluble as possible. If the copolymerization of acrylamide with other water-soluble monomers presents no special problems, difficulties sometimes arise when the comonomer is water-insoluble. In particular the molecular weight is often limited

- the obtained copolymer must be as similar as possible to the pure polyacrylamide. In other words, it must contain less of 0.1% of coloured monomer

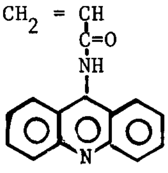
- the synthesis of the comonomer must be easy and his chemical structure must be as near as possible of acrylamide and contain no reactive groups able to interact during the copolymerization or to induce specific interactions on the polymeric chain

- finally, if hydrolysed samples of polyacrylamides are needed, it is necessary than the coloured group is not cleaved during the hydrolysis reaction.

Various coloured monomers have been already prepared from acryloyl chloride (EISELE et al., 1961 ; DREYFUS and MARCHAL, 1975). For our purpose, the best results have been obtained with acrylic monomers of 2,4 dinitrophenylhydrazine (1), 1-amino-anthraquinone (2) and 9-aminoacridine (3).



(1)



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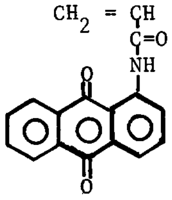

(2)

However, only the copolymers of (1) with acrylamide (HPAM-DNA) have been extensively prepared and used in our adsorption study. For this reason the present report will be exclusively focused on it.

EXPERIMENTAL

Synthesis of N-2,4 dinitroaniline-acrylamide (1)

11g (0.05 mol) of 2,4 dinitrophenylhydrazine (MERCK) was added to 7 ml (0.05 mol) of triethylamine in 100 ml of anhydrous THF. 11 ml (0.05 mol) of acryloyl chloride (FLUKA) was added dropwise under stirring to the solution maintained to 0°C. After one hour the solution was filtered, then THF was evaporated and the yellow residue was washed with a little amount of water and dried. 8.5g (67% yield) of (1) was obtained after one recrystallization in a mixture of THF/CH_3OH. m.p. 157°C. It has been characterized by NMR in DMSO, spectroscopy in THF and elemental analysis.

Copolymerization with acrylamide (HPAM-ADN 0%)

An example of copolymerization procedure was as follows. 40 mg (0.16 mmol) of (1) was dissolved in 20 ml of hot THF and added to a solution of 35,5g (0.5 mol) of acrylamide in 400 ml of freshly distilled water. The mixture was stirred under a nitrogen atmosphere at 50°C. 60 mg of potassium persulfate was added. After 3 hours the polymer is recuperated by precipitation in methanol and purified by a second precipitation in a mixture THF/CH_3OH. After washing with methanol, and drying under vacuum 15,3g (43% yield) of polymer was obtained.$[\eta]$: 6 dl/g in water (0.1 M NaCl) - M_η : $2.5x10^6$ ($G = 1500\ s^{-1}$).

Hydrolysis (HPAM-ADN X%)

To a solution of 6,75g of NaOH dissolved in 50 ml of distillated water and maintained at 63°C, was added under stirring a solution of 6g of copolymer dissolved in 450 ml freshly distillated water. After 10 min 250 ml (a) of the solution was taken off and the remaining (b) after 50 mn. The pH was quickly adjusted to 7-8 and the polymers were recuperated above. 2.9g and 2.1g were respectively obtained (88% yield). They were characterized by elemental analysis, spectroscopy and viscosity. (a) % hydrolysis : 17%, $[\eta]$: 9.6 dl/g ; (b) % hydrolysis : 38%, $[\eta]$: 15,2 dl/g.

All the obtained copolymers have been fractionated and characterized by classical methods (GPC, light scattering, viscosimetry) (FRANCOIS et al., 1979). Spectroscopic measurements were realized with a Beckman Acta IV equipment.

RESULTS AND DISCUSSION

In the UV-visible spectra of the obtained coloured polymers, maxima of absorption were observed which were characteristic for the dyes. This shows that the dyes are incorporated into the macromolecular chains. In Fig. 1 the adsorption spectra for the unfractionated copolymer (HPAM-ADN 0%) are reproduced for two pH. The study as a function of the concentration in copolymer, shows that the Lambert-Beer's law is well obeyed in the studied range (up to 1000 ppm) and leads to $\varepsilon = 3.3\ M^{-1}$ at pH 5 ($\lambda_{max} = 360$ nm) and $4.05\ M^{-1}\ cm^{-1}$ at pH 9 ($\lambda_{max} = 415$ nm). Compared with the results obtained for the 2,4 dinitrophenylhydrazine in the same conditions ($\varepsilon' = 11300\ M^{-1}\ cm^{-1}$ at pH 5, $\lambda_{max} = 360$ nm) we obtain a mole content of dye in the copolymer of 1/3424 which is 91% of the total dye engaged in the synthesis. Considering the high molecular weight (2.5×10^6) and the yield (88%) obtained, we conclude that the polymerization of acrylamide in presence of such quantities of coloured monomer, does not change apparently the efficiency of the polymerization. From this polymer six fractions have been obtained and the ε values

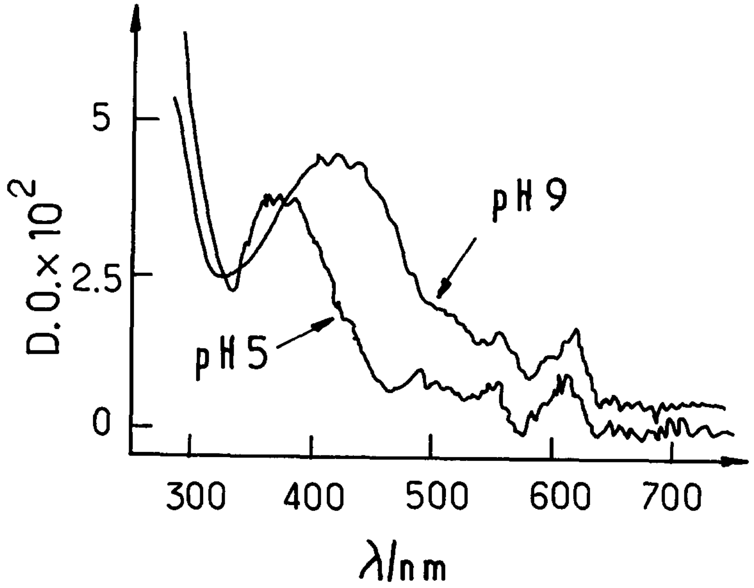

Figure 1 : Absorption spectra of HPAM-ADN 0% in water (100 ppm - 0.1 M NaCl)

determined for each, are quite comparable (ε = 4.05 ± 0.1 M^{-1} cm^{-1}). This clearly indicates that the composition of the copolymer is uniform and independent of the degree of polymerization. In addition the behaviour of the hydrolyzed samples is quite similar to the unhydrolyzed : we have found ε = 3.89 ± 0.1 M^{-1} cm^{-1} for HPAM-ADN 17% and ε = 4.07 ± 0.1 M^{-1} cm^{-1} for HPAM-ADN 38%. It is concluded that the dye has not been affected by the hydrolysis.

All the obtained results show that this type of coloured polymer is very suitable to do quantitative analysis of polyacrylamide in water. The colorimetric method has the great advantage to be very easy. In our standard conditions, concentrations in polymer of 5 x 10^{-2} g/l can be detected with a precision better than 5%.

The principle of this method can be extended to commercial polyacrylamides by grafting on some amide groups a dye with an aldehyde function or by using the Mannich reaction including first the usual methylolation reaction and subsequently the treatment with a amino-dye (SCHILLER and SUEN, 1956).

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