

## SYNTHESIS OF POLYACRYLAMIDE - BASED HYDROGELS BY SIMULTANEOUS POLYMERIZATION/CROSSLINKING

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Received January 15, 2007

A simultaneous polymerization/crosslinking method for preparing polyacrylamide – based hydrogels is proposed. The influence of different experimental parameters (chemical nature of the crosslinking agent, pH, monomer and initiator concentration, temperature and reaction time) on crosslinked polymer yield and its swelling behavior was studied. Both polymer yield and network structure – as reflected by its swelling capacity – depend on synthesis conditions and mainly on monomer concentration in the initial monomer solution.

### INTRODUCTION

A large variety of hydrogels were obtained from many suitable monomers. Their properties depend on the chemical nature of the starting compounds and the crosslinking degree of the resulting polymeric networks. They satisfy the requirements imposed by different applications in food industry, cosmetics, agriculture, medicine, pharmacy, technical and electronic instrumentation, photography etc.

The main property of hydrogels stands in their capacity to absorb large amounts of water. This characteristic depends on network structure, determined by the experimental conditions used for their preparation of polymer gels.<sup>1</sup>

Earlier investigations were concerned with the hydrophilic nature and the swelling ability of hydrogels. Gradually, the investigation area was extended and mechanical, diffusion and absorption properties became of real interest since they confer these materials the capacity to mime living tissues.

Last years, many papers reported the preparation and swelling behavior of polyacrylamide (PAAm) based hydrogels, which are of both theoretical and practical interest.<sup>2-9</sup> Usually, these materials are obtained by copolymerization of acrylamide (AAM) with a bifunctional monomer, or by free radical

polymerization of AAm followed by crosslinking of the resulted homopolymer.<sup>9-11</sup> The present paper proposes the synthesis of PAAm – based gels by a simultaneous polymerization/ crosslinking method in presence of aliphatic aldehydes as crosslinking agents. The influence of experimental parameters on both polymerization yield and swelling behavior of hydrogels are discussed.

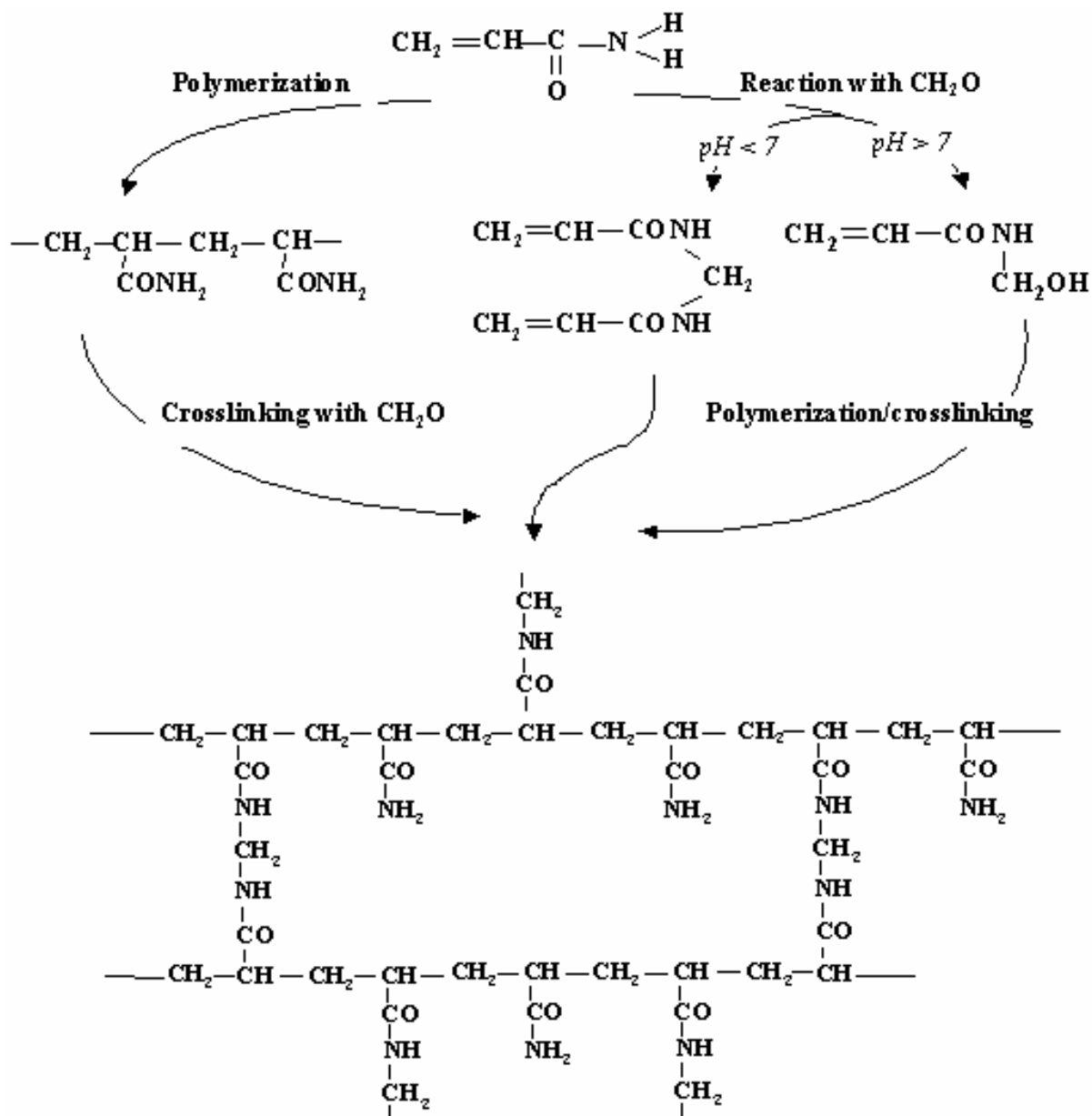
### RESULTS AND DISCUSSION

The reaction of AAm with formaldehyde in basic media is well known and largely used in practice.<sup>12</sup> It forms methylol-acrylamide which, in certain conditions, turns in N,N'-methylenebis(acrylamide), usually used as crosslinking agent in polymerization reactions.

It is worth mentioning that the methylation can be carried out, also, in polymer analogous reactions between pre-synthesized PAAm and formaldehyde in alkaline media. The obtained products are expected to crosslink in proper conditions, forming a gel structure.

Based on these considerations it was interesting to undergo the preparation of PAAm - based gels by a simultaneous polymerization/crosslinking procedure of AAM in the presence of aldehydes (Scheme I).

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Scheme 1 – Schematic representation of the simultaneous polymerization/crosslinking of AAm.

Formaldehyde, butyraldehyde and 2,4-dihydroxybenzaldehyde were tested as crosslinking agents, at two pH values (a low acid, pH = 5.5 – 6 and a low basic, pH = 9.5) realized with Na<sub>2</sub>CO<sub>3</sub> buffer. The progress of the reaction was followed determining the polymer yields and swelling degrees. Reasonable polymer yields were obtained with formaldehyde in basic conditions (Table 1); this compound is more reactive as compared to the other aliphatic or aromatic aldehydes in forming methyloic intermediates. The high swelling degree of the products obtained in the presence of formaldehyde denote that the crosslinking has occurred to a lesser extent.

The polymerization of AAm in presence of butyraldehyde in basic media yields water-soluble PAAm, which might suggest that no crosslinking occurs. At the same time, 2,4-dihydroxybenzaldehyde forms low swelling capacity products, unable to be used in hydrogel specific applications.

The evolution of the polymerization/crosslinking reaction in presence of formaldehyde is strongly influenced by pH. In basic conditions the polymer yield reaches 50 %, the obtained gel presenting a swelling degree of about 400 %. In slight acid media the prepared hydrogels swell up to 9.000%. One has to consider the formation, in acid media, of low amounts of methylenebis(acrylamide), able to copolymerize with AAm in a less structured tridimensional network.

Table 1

Influence of crosslinking agent, at acid and basic pH values, on crosslinked polymer yield

No.	Aldehyde	pH	Crosslinked polymer yield (%)
1	CH <sub>2</sub> O	5.5 – 6.0	35.13
2		9.5*	52.16
3	C <sub>3</sub> H <sub>7</sub> -CHO	5.5 – 6.0	11.63
4		9.5*	---
5	C <sub>6</sub> H <sub>5</sub> (OH) <sub>2</sub> CHO	5.5 – 6.0	11.14
6		9.5*	8.25

[AAm] = 3 (mol/L), [K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>]/[AAm] (mol/mol) = 0.055, [aldehyde]/[AAm] (mol /mol) = 3/1, temperature = 50 °C, reaction time = 5 h, \*buffer = Na<sub>2</sub>CO<sub>3</sub> ( 0.53 %)

Normally, pH modification shouldn't affect the tridimensional network structure obtained through the polymerization/crosslinking process. No matter the chemical nature of the intermediate compounds and no matter the succession of elementary reactions, the hydrogels structure should be the same (Scheme 1).

The experimental data on the influence of monomer and initiator concentrations, temperature and reaction time reveal that polymer yields do not overpass 50 % (Figs. 1 – 4). This is probably due to the formation of a mixture of linear PAAm and crosslinked product, during the polymerization/crosslinking process, from which the former one is

eliminated through successive extractions during the hydrogel purification.

Monomer concentration is the parameter that affects the polymer synthesis. Both polymer yield and network structure depend on initial monomer concentration (Table 2), as previously observed in different papers.<sup>8,9</sup>

The modification of initiator concentration ([I<sub>2</sub>] = 0.094 – 0.85 %), even in large limits, of temperature (T = 33 – 61°C) and polymerization duration (t = 1 – 7 hs), determine minor changes in polymer yield (Figs. 2 – 4). Also, initiator concentration has no relevant influence on the swelling behavior of the hydrogels (Table 3).

Table 2

Influence of initial monomer concentration on polymer swelling behaviour

No.	[AAm] (mol/l)	Swelling degree (%)	Swelling rate constant (min <sup>-1</sup> )
1	0.56	3880	2.08·10 <sup>-4</sup>
2	1.40	4870	7.178·10 <sup>-5</sup>
3	2.24	9100	6.028·10 <sup>-5</sup>

[K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>], 0.5 %; [CH<sub>2</sub>O] = 12.33 mol/L, pH = 5,5 –6; temperature = 50 °C; reaction duration =4 h

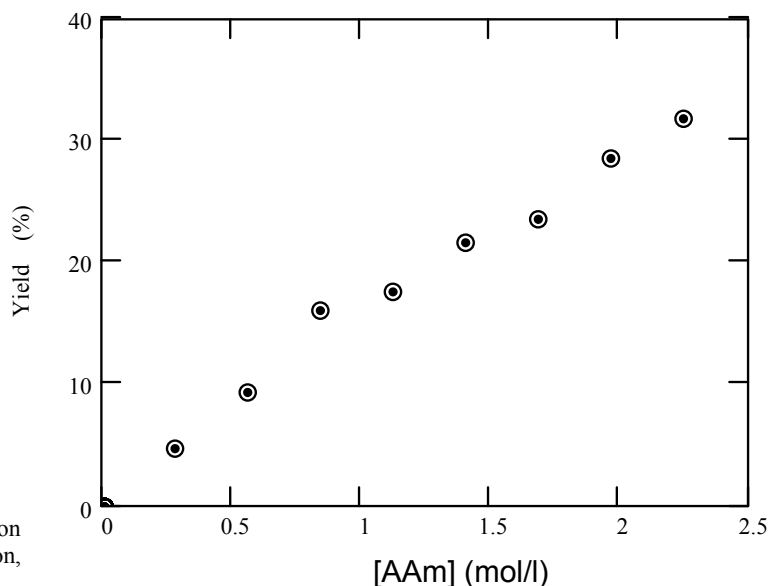


Fig. 1 – Influence of monomer concentration on polymer yield. Temperature, 50 °C; reaction duration, 4 h; [I<sub>2</sub>], 0.5 %; [CH<sub>2</sub>O] = 12.33 mol/L.

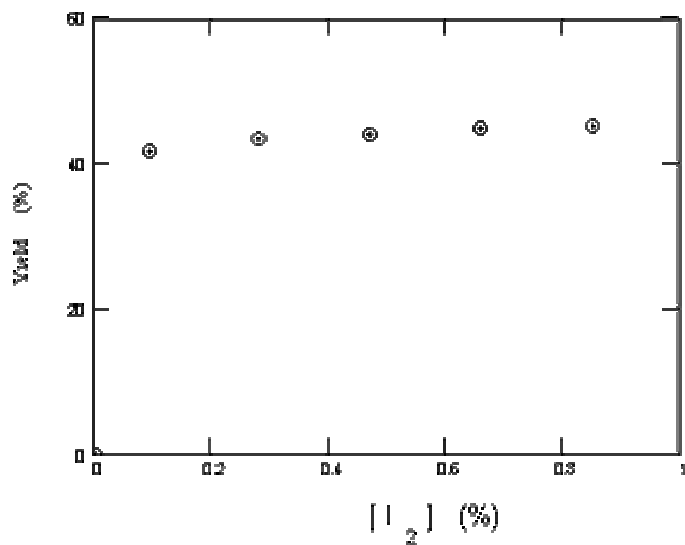


Fig. 2 – Influence of initiator concentration on polymer yield. [AAm], 3 mol/L; [Aldehyde]/[AAm], 3/1 mol/mol; [I<sub>2</sub>], K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>; temperature, 50 °C; reaction duration, 5 h.

Fig. 3 – Influence of reaction temperature on polymer yield. [AAm], 3 mol/L; [I<sub>2</sub>], 0.28%; [Aldehyde]/[AAm], 5/1 mol/mol; reaction time, 4 h.

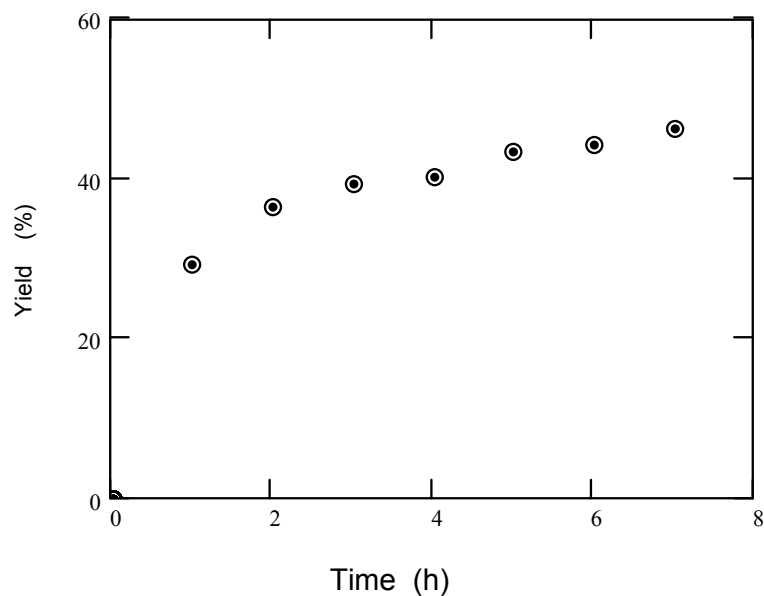
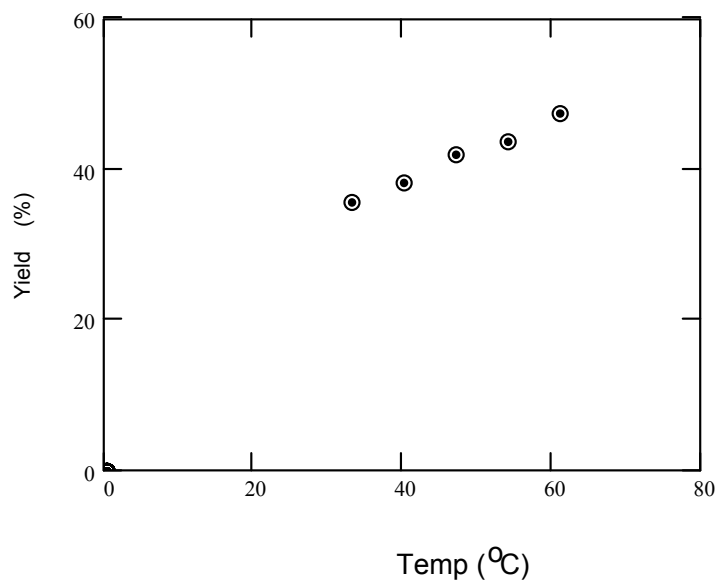


Fig. 4 – Influence of polymerization duration on polymer yield. [AAm], 3 mol/L; [I<sub>2</sub>], 0.28%; temperature, 50 °C; [CH<sub>2</sub>O]/[AAm], 5/1 mol/mol.

Table 3

Influence of initiator concentration on polymer swelling behaviour

No.	[I <sub>2</sub> ] (%)	Swelling degree (%)	Swelling rate constant (min <sup>-1</sup> )
1	0.094	1100	4.4·10 <sup>-4</sup>
2	0.470	930	2.7·10 <sup>-4</sup>
3	0.850	1020	1.3·10 <sup>-4</sup>

[AAM], 3 mol/L; [Aldehyde]/[AAM], 3/1 mol/mol; [I<sub>2</sub>], K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>; temperature, 50 °C; reaction duration, 5 h; pH = 5,5 –6.

The processing of the experimental swelling data yielded curves having shapes as presented in figure 5. The resulting data, obtained from representation of this type, are given in Tables 2 and 3.

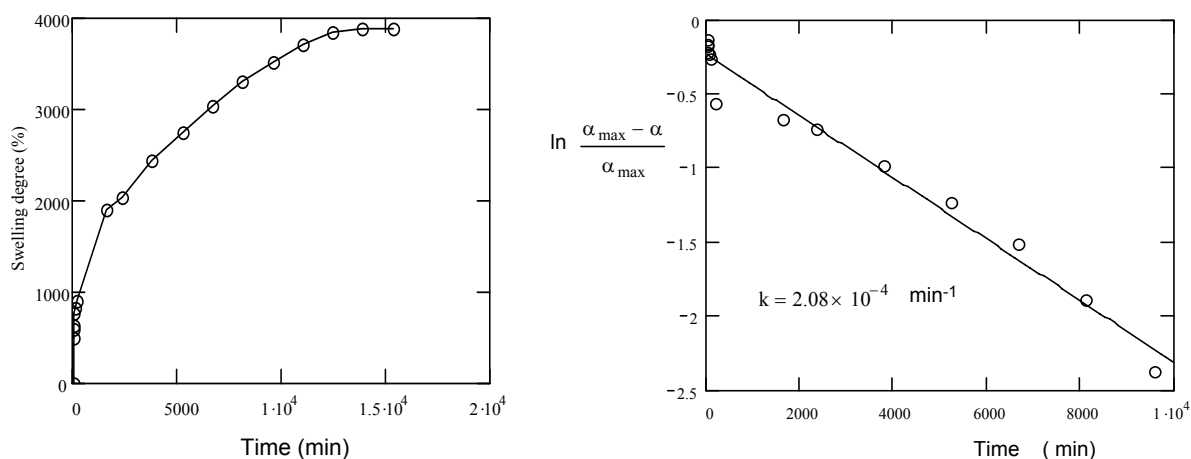


Fig. 5 – Typical swelling kinetic curves (sample No. 1, Table 2).

## EXPERIMENTAL

### Materials

Acrylamide (Merck) was recrystallized from acetone/methanol mixture (7/3 v/v) and dried in vacuum. Formaldehyde, 37% solution (Chemical Company, Roumania), butyraldehyde (B.D.H. Laboratory, Chemicals Division, England) and 2,4-dihydroxybenzaldehyde (Fluka), all pure chemical reagents, were used as delivered.

Potassium peroxodisulfate was purified just before use by the usual method.

### Procedure

The preparation of PAAm-based hydrogels was achieved by an original polymerization/crosslinking procedure.

The reactions were carried out in a three-bottomed flask in water, under nitrogen, at pre-established temperature, duration and monomer, initiator and crosslinking agent concentrations. The temperature was maintained with an accuracy of  $\pm 0.5^\circ\text{C}$ . At the end of the reaction the product was extracted in water, to remove the non-reacted monomer and the homopolymer. Subsequently, water in the polymer network was replaced with methanol and the product dried to constant weight at  $40^\circ\text{C}$ .

The polymer yield was determined gravimetrically, the same technique being used to follow the evolution of the polymerization process. Several experiments were performed to check the accuracy/reproducibility of the experimental data.

### Swelling

The swelling of PAAm-based materials in water was studied with a Dogatkin type apparatus, at room temperature. The swelling degree ( $\alpha$ ) was determined according to

$$\alpha = (W_w/W_p) \times 100$$

where  $W_w$  represents the weight of absorbed water and  $W_p$  the weight of the dry polymer.

The swelling rate constant was evaluated from the semi-logarithmic plots of the swelling degree vs. time, by using the Math Cad 7 Professional program.

## CONCLUSIONS

A simultaneous polymerization/crosslinking method to prepare PAAm-based hydrogels is proposed. The obtained stable networks were

characterized determining the swelling degrees that are placed in the range of those specific to super absorbent hydrogels.

Both polymer yield and swelling behavior depend on chemical structure of the aldehyde crosslinking agent and on medium pH.

The hydrogels crosslinking degree, as reflected by their swelling ability, depends on synthesis conditions. The most important parameter affecting the swelling behavior was found to be the initial concentration of the monomer.

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