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Crosslinking reactions and swelling behavior of matrices based on N-acryloyl-TRIS(hydroxymethyl)aminomethane

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Summary

In this study, new hydrogels in rod shape were prepared from N-acryloyl-TRIS(hydroxymethyl)aminomethane (NAT) using ethylene glycol dimethacrylate (EGDMA) or N,N'methylenebisacrylamide (BIS) as crosslinking agent, dimethylformamide (DMF) as solvent and benzoyl peroxide (BPO) as initiator. In most cases, 2-hydroxyethyl methacrylate (HEMA), acrylamide (Aam) or acrylic acid (Aac) were used as co-monomers. The polymeric matrices obtained by free radical polymerization exhibited different properties by changing crosslinker, crosslinker concentration, co-monomer and initial NAT/co-monomer mole ratio. Besides, hydrogels from HEMA, Aam and Aac with BIS in absence of NAT were prepared under the same experimental reaction conditions in order to compare the properties of these products with those synthesized from NAT and the respective co-monomers. Some of the final products were selected to perform urea release assays, conducted through swelling-controlled release. Urea was chosen as "model" plant fertilizer agent.

Introduction

Hydrogels are network polymeric materials that exhibit the ability to absorb huge volumes of water, by swelling and not dissolving.
The liquid prevents the network from collapsing into a compact mass while the network prevents the liquid from flowing away. They consist of hydrophilic crosslinked macromolecules forming a three-dimensional and tangled network. The properties of hydrogels are dependent upon different factors as: their method of preparation, presence of functional groups, network elasticity, cross-linking degree, composition of network by the presence of co-monomer, network-water interaction and distinct possibility of arrangements between hydrophobic-hydrophilic domains [1-5]. Those have received attention in the past few years as materials for biological, biomedical, pharmaceutical and agricultural applications, though much attention is focused on their use as a controlled release system for drugs, bioactive agents or pesticides, incorporating them into a hydrogel as carrier [1, 6-8]. In agricultural applications, once bioactive agents have been released, the hydrogel is retained in the soil where it has the ability to hold and retain water thus serving as reservoir and

promoting optimal plant growth. For these applications, the swelling and the diffusion processes are very important since the former involves the segment movements that enlarge the separation distances between chains while the last permits the migration of water to pre-existent spaces between chains.

NAT monomer (Figure 1) was previously used in preparation of multifunctional poly(acrylamides) [9] and gels for electrophoresis and isoelectric focusing by using BIS as cross-linking agent [10] and in formation of poly(NAT) hydrophobically modified with adamantyl groups and a β-cyclodextrin polymer [11]. Additionally, it was used to synthesize Trisacryl using N,N´diallyltartradiamide as cross-linking agent, [12] as affinity chromatography base support and as microspheres for therapeutic embolization [13-15]. In this work, the advantageous properties of NAT monomer were taken into account to synthesize new different hydrogels, providing hydroxymethyl triads attached as side groups to backbone chains that confer hydrophilicity to the final crosslinked structures. So, highly swollen matrices in rod form were prepared by polymerization of NAT or co-polymerization with HEMA, Aam or Aac with crosslinkers. The influence of changing crosslinker, crosslinker concentration, co-monomer and initial NAT / co-monomer mole ratio on the swelling properties, water diffusional behavior and hydrogel systems network properties were examined.
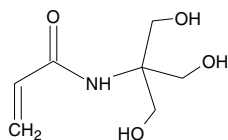
Figure 1: N-acryloyl-TRIS(hydroxymethyl)aminomethane

Experimental

Reagents and equipment

The following chemicals were purchased and used: N-acryloyl-TRIS (hydroxymethyl) aminomethane (NAT) (Aldrich)(Steinheim,Germany); 2-hydroxyethyl methacrylate (HEMA) (95 %) (Fluka) (St.Louis, USA); acrylamide (Aam) (Fluka) (St.Louis, USA); acrylic acid (Aac) (Basf) (Argentine); N,N'methylenebisacrylamide (BIS) (Mallinckrodt) (Kentucky, USA); ethylene glycol dimethacrylate (EGDMA), (90 %) (Fluka) (St. Louis, USA); benzoyl peroxide (BPO), (Fluka) (Switzerland) (purified by crystallization from methanol); dimethylformamide (DMF) (p.a.) (Cicarelli) (Argentine) purified through vacuum distillation (84°C / 90 mm Hg); distilled water; urea (Anedra) (Argentine) and p-dimethylaminobenzaldehyde (DMAB) (Anedra) (Argentine). The UV-Visible spectra were recorded with a Shimadzu recording spectrophotometer UV-260.

Matrices synthesis

All matrices were prepared by free-radical cross-linking polymerization. A typical procedure for co-polymerization can be described as follows: the monomer or a mixture of monomers and cross-linking agents (Table 1) were dissolved in DMF (10 mL) in glass tubes (14 mm internal diameter and 15 cm long) used as

polymerization reactor. Then, BPO (0.02 g) was added to each solution followed by stirring for 75 min with an ultrasonic bath and left to react for 2.5 h at 80°C. After breaking the tubes, the yielded matrices in long cylindrical shapes were cut into pieces and immersed twice in a large excess of distilled DMF at room temperature for 24 h, dried under vacuum to constant weight, and stored at room temperature.

The molar compositions of the initial solutions state to obtain the products are shown in Table 2. Besides, it can be seen the total co-monomers moles as well as the ratio R calculated as follow (Equation 1):

$$R = \text{moles of BIS / total co-monomers moles} \tag{1}$$

Swelling and diffusion experiments

Dried samples were placed in distilled water and kept at room temperature in order to determine their swelling behavior. Swollen samples removed from the water bath at regular intervals were superficially dried with tissue paper, weighed by an electronic balance and placed in the same bath. The measurements were made until a constant weight was achieved for each sample. The equilibrium weight swelling ratio q_w was calculated as Equation 2:

$$q_w = \text{swollen mass / dry mass} \tag{2}$$

For the swelling curves, q_w values at each time were plotted versus time (min).

To determine the nature of diffusion of water into matrices, the following Equation (3) was used:

$$F = M_t/M_\infty = k\,t^{\,n} \tag{3}$$

where M_t denotes the amount of water diffused into the matrix at time t (swollen mass at time t - dry mass) while M_∞ corresponds to the amount of water diffused into the matrix at infinity, at equilibrium, (swollen mass at equilibrium - dry mass), k is a constant related to the structure of the network, and the exponent n is a number to determine the type of diffusion. For the matrices, this equation (3) is applied to the initial stages of swelling and plots of $ln\,F$ versus $ln\,t$ yield straight lines up to almost 60 % increase in the mass of each hydrogel. So, $ln\,F$ versus $ln\,t$ plots were drawn using the kinetics of swelling after which n and k values were calculated from the slopes and intercepts of the lines, respectively.

Urea release from hydrogels

Hydrogel samples (500 mg): poly (NAT-BIS) 1, poly (NAT-Aam-BIS) 1, poly (NAT-Aac-BIS) 1, poly (NAT-HEMA-BIS) 1, poly (NAT-Aam-BIS) 2, poly (NAT-Aac-BIS) 2 and poly (NAT-HEMA-BIS) 2, were swollen with 0.5 mL of an urea aqueous solution (10 g /100 mL) in a tube, allowing enough time for the drug to diffuse into the gel. After imbibitions, the samples were dried to constant weight and put into the tubular cell separated by a dialysis membrane from the recipient containing distilled water (25 mL), under stirring at room temperature. Aliquots (1 mL) were removed periodically from the release solution and urea amount was determined. For this, each urea sample (1 mL) was diluted to 5 mL from which 1 mL was taken and mixed with 2 mL of DMAB solution (it was prepared using 1.6 g/100 mL ethanol after which 10 mL of HCl were added) and left for 10 min at 25°C. Next, the absorbance values were measured at $\lambda = 420$ nm using a UV-Visible spectrophotometer. The final urea

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concentration from aliquots was then calculated using the extinction coefficient obtained from an appropriate calibration plot. So, taking into account the initial urea amount into the gels (50 mg) and the urea released at each time, a percentage (%) versus time (min) was plotted.

In all cases, each aliquot (1 mL) removed periodically (to determine the amount of urea released) was replaced by distilled water (1 mL). So, the volume in the solution was always 25 mL. The actual values of urea were corrected in all cases according to the urea removed in all aliquots.

Table 1: Experimental conditions to yield hydrogels from NAT and results of q_w and n values from products

Product	NAT (g)	co-mono-mer	co-mono-mer (g)	crosslin-king agent	crosslinking agent (g)	q_w^a	n
Poly (NAT-BIS) 1	2.0	-	-	BIS	0.24	4.8	0.68
Poly (NAT-BIS) 2	2.0	-	-	BIS	0.36	3.7	0.62
Poly (NAT-BIS) 3	2.0	-	-	BIS	0.48	3.4	0.63
Poly(NAT-EGDMA) 1	2.0	-	-	EGDMA	0.24	4.4	0.83
Poly(NAT-EGDMA) 2	2.0	-	-	EGDMA	0.36	3.2	0.76
Poly(NAT-EGDMA) 3	2.0	-	-	EGDMA	0.48	2.9	0.77
Poly(NAT-Aam-BIS) 1	1.8	Aam	0.2	BIS	0.24	5.1	0.58
Poly(NAT-Aam-BIS) 2	1.6	Aam	0.4	BIS	0.24	5.9	0.61
Poly(NAT-Aam-BIS) 3	1.4	Aam	0.6	BIS	0.24	6.8	0.60
Poly (NAT-Aam-BIS)[b] 4	1.0	Aam	1.0	BIS	0.24	18.0	-
Poly (Aam-BIS)[c]	-	Aam	2.0	BIS	0.24	-	-
Poly (NAT-Aac-BIS) 1	1.8	Aac	0.2	BIS	0.24	7.9	0.69
Poly (NAT-Aac-BIS) 2	1.6	Aac	0.4	BIS	0.24	8.4	0.66
Poly (NAT-Aac-BIS) 3	1.4	Aac	0.6	BIS	0.24	5.3	0.59
Poly (NAT-Aac-BIS) 4	1.0	Aac	1.0	BIS	0.24	5.9	0.59
Poly (Aac-BIS)	-	Aac	2.0	BIS	0.24	7.0	0.51
Poly(NAT-HEMA-BIS) 1	1.8	HEMA	0.2	BIS	0.24	4.7	0.73
Poly(NAT-HEMA-BIS) 2	1.6	HEMA	0.4	BIS	0.24	4.7	0.68
Poly(NAT-HEMA-BIS) 3	1.4	HEMA	0.6	BIS	0.24	4.9	0.61
Poly(NAT-HEMA-BIS) 4	1.0	HEMA	1.0	BIS	0.24	4.0	0.53
Poly (HEMA-BIS)	-	HEMA	2.0	BIS	0.24	1.8	0.48

a) Equilibrium weight swelling ratio
b) Product obtained in powder solid form
c) Soluble product

Results and discussion

Matrices synthesis

In this study, free radical polymerization processing was used for the development of new gel-like materials derived from NAT monomer. In preliminary reactions assayed between NAT and BIS, no solid products were obtained when 0.03 or 0.12 g of BIS was used. So, a few more reactions were performed using 0.24-0.48 g of BIS.

Products presented in Table 1, except poly (NAT-Aam-BIS) 4 and poly (Aam-BIS), were obtained in rod form. Product poly (NAT-Aam-BIS) 4 was obtained in powder solid form while a soluble product was obtained in the experimental reaction condition assayed for poly (Aam-BIS).

The products were purified by immersion in a large excess of distilled DMF to remove any un-reacted monomers or initiator within the matrices.

In the preparation of products, the crosslinker, crosslinker concentration, co-monomer and initial NAT / co-monomer mole ratio were modified. The conditions for both matrices production are summarized in Table 1. These samples were used in experiments of swelling and diffusion.

Swelling experiments

Product swelling behaviors were gravimetrically measured. The q_w parameter is the swelling reached by the hydrogel until the equilibrium between water capacity to separate and to stretch the chains and the elastic force generated was reached. The crosslinker concentration effect on the swelling behavior of poly (NAT-EGDMA) (1-3) and poly (NAT-BIS)(1-3) products is given in Figs 2-3, respectively. In these experiments, crosslinker concentration was varied. The total monomer concentration and NAT / crosslinker mole ratio were set. It was shown that a rise in the crosslinking density, which increases with the concentration of the cross-linking agent in both cases, results in a decrease in the distance between the macromolecular chains, the size of pores will be smaller, the flexibility of the chains will be less and the amount of water retained by the hydrogel and q_w will decrease (Table 1).
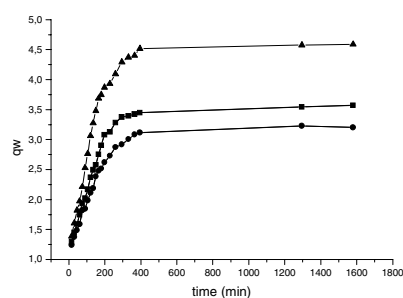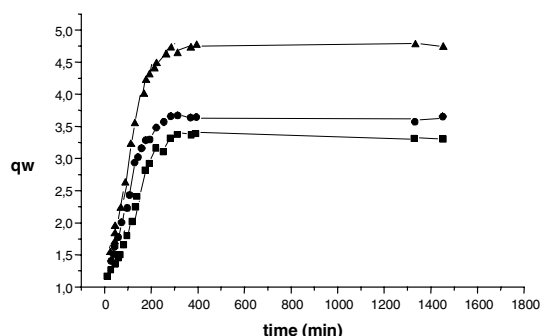

Figure 2: Swelling kinetic from Poly(NAT-EGDMA)1 (▲), Poly(NAT-EGDMA)2 (■) and Poly(NAT-EGDMA)3 (●)

In fact, it has been found that higher swelling rate is reached in each system when lesser crosslinker agent enters into the hydrogel (Figs. 2-3). Less crosslinking degree could permit more porous network structure and higher water diffusivity and migration. As can be seen in Figures 2-3, the q_w values increased with time until a constant value (equilibrium weight swelling ratio) for all products shown in Table 1. BIS crosslinked agent was the agent of choice because it yielded slightly more swellable networks structures.

By varying the co-monomer (Aam, Aac and HEMA) and the monomer mixture ratio respect to hydrogels derived from NAT, the effect of their presence on the swelling behavior was studied. Hence, BIS was established as crosslinked agent in a fixed concentration. Swelling behavior of hydrogels obtained with distinct monomer and initial NAT/co-monomer mole ratio was studied (Tables 1 and 2).

Besides, hydrogels from HEMA, Aam and Aac with BIS but without NAT were prepared under the same experimental conditions in order to compare the properties of these products with those synthesized from NAT and the respective co-monomers.

Figure 3: Swelling kinetic from Poly(NAT-BIS)1(▲), Poly(NAT-BIS)2 (●) and Poly(NAT-BIS)3 (■)

Table 2: Molar compositions of the initial solutions state to obtain the products, total co-monomers moles values and R

Product	NAT (mol 10^{-3})	co-monomer (mol 10^{-3})	Total moles (NAT and co-monomer) (mol 10^{-3})	crosslinking agent (mol 10^{-3})	R	q_w
Poly (NAT-BIS) 1	11.42	0	11.42	1.56	0.136	4.8
Poly(NAT-Aam-BIS) 1	10.28	2.81	13.10	1.56	0.119	5.1
Poly(NAT-Aam-BIS) 2	9.14	5.63	14.77	1.56	0.106	5.9
Poly(NAT-Aam-BIS) 3	8.00	8.44	16.44	1.56	0.095	6.8
Poly (NAT-Aam-BIS) 4	5.71	14.07	19.78	1.56	0.079	18.0
Poly (Aam-BIS)	0	28.14	28.14	1.56	0.055	-
Poly (NAT-Aac-BIS) 1	10.28	2.78	13.06	1.56	0.119	7.9
Poly (NAT-Aac-BIS) 2	9.14	5.56	14.70	1.56	0.106	8.4
Poly (NAT-Aac-BIS) 3	8.00	8.33	16.33	1.56	0.096	5.3
Poly (NAT-Aac-BIS) 4	5.71	13.88	19.60	1.56	0.080	5.9
Poly (Aac-BIS)	0	27.75	27.75	1.56	0.056	7.0
Poly(NAT-HEMA-BIS) 1	10.28	1.54	11.82	1.56	0.132	4.7
Poly(NAT-HEMA-BIS) 2	9.14	3.07	12.21	1.56	0.128	4.7
Poly(NAT-HEMA-BIS) 3	8.00	4.61	12.61	1.56	0.124	4.9
Poly(NAT-HEMA-BIS) 4	5.71	7.68	13.39	1.56	0.117	4.0
Poly (HEMA-BIS)	0	15.37	15.37	1.56	0.101	1.8

In Table 2, it can be seen the molar compositions of the initial solutions state to obtain the products, the total co-monomers moles and R. In the cases of NAT-Aam-BIS and NAT-Aac-BIS-containing products, it can be observed that total co-monomers moles are equal since Aam and Aac present similar molecular weights (Mw Aam = 71.08; Mw Aac = 72.06). In both cases, R resulted similar and decreases while the amount of Aam or Aac increases. In spite of this situation, these products reached different values of q_w. This show that the equilibrium weight swelling ratio was strongly influenced by the presence of each co-monomer since the theoretical value of crosslinking amount is similar (1.56 10^{-3} moles in all cases).

In the case of NAT-HEMA-BIS-containing products, it can be seen that R resulted high than those from NAT-Aam-BIS and NAT-Aac-BIS-containing products

indicating major possibility of crosslinking and corroborated by their low q_w values. Notwithstanding, poly(HEMA-BIS) presented the lower R (minor crosslinks) and the minor q_w (low entrance of water) values respect NAT-HEMA-BIS-containing products, which suggested for the last, the enhance of hydrophilicity due at the presence of NAT.

By another way, comparing poly(NAT-Aam-BIS)1, poly(NAT-Aac-BIS)1 and poly(NAT-HEMA-BIS)4 that presented similar both R values (0.119; 0.119 and 0.117, respectively) and theoretical possibility of crosslinking but different q_w values (5.1; 7.9 and 4.0, respectively), it can be concluded that the hydrogels swellability is influenced by the co-monomer present in the samples.

In general, both factors: an increase in the amount of Aam incorporated into the copolymers poly (NAT-Aam-BIS) and the minor possibility of crosslinks (by decrease in R), increases the overall matrices hydrophilicity (an increase in q_w values was evidenced; Table 1) possibly due to a better combination of functional hydrophilic groups as centers for hydrogen bonding sites as Aam amount increases into the matrix. On the other hand, an increase in HEMA incorporation in poly (NAT-HEMA-BIS) involving little variations in R, does not change or decrease the swelling relative to poly (NAT-BIS) 1. This last behavior could be due to the fact that the hydroxymethyl triad/amide repetitive unit drops as soon as the hydroxyethyl group belonging to HEMA rises, diminishing the total hydrophilic groups into the hydrogels. Besides, the presence of Aam or HEMA into the copolymers decreases the rate of water uptake relative to poly (NAT-BIS) 1.

An abnormal final behavior was observed with poly (NAT-Aac-BIS) products: in the first assays, the q_w values appeared high but varied (dropping the value) after the drying process when the same samples were dried and re-swelled in later assays. In these cases the swelling behavior was influenced by the gels "history" [2]. Thus, after a sample was totally swelled (in the first assay) dried and re-swelled, a collapse could be noticed possibly due to irreversible changes by physical crosslinks since could exist hydrogen bonding and van der Waals interactions between functional pendent groups amongst vicinal chains. This last behavior resulted in accordance with that reported previously by another author [16] based on studies of poly (acrylamide-co-acrylic acid) hydrogels properties.

Therefore, it can be seen that an increasing content of Aac from 0 to 20 % into the products, results in an increase in q_w. After this, an increase in the carboxyl groups content, leads to a decrease in q_w values, probably due to a stabilization in the system caused by those intra and inter molecular interactions.

Poly (Aam-BIS) resulted in a soluble product under the experimental conditions assayed. Nevertheless, poly (Aac-BIS) and poly (HEMA-BIS) were collected in rod form and presented the following final q_w values: 7.0 and 1.8, respectively.

From all products, NAT-Aam-BIS-containing hydrogels presented the best combination between good swelling values and slow kinetics. Figure 4 shows, as an example, the initial stage (until 3500 min) of typical swelling kinetic curves from poly(NAT-Aac-BIS)2, poly(NAT-HEMA-BIS)2 and poly(NAT-AAm-BIS)2.

In general, it can be concluded that the incorporation of NAT into the products, enhances the swelling properties in HEMA-BIS-containing hydrogels. On the other hand, the Aam and Aac incorporation and combination into the products improved the swelling properties in NAT-BIS-containing hydrogels.
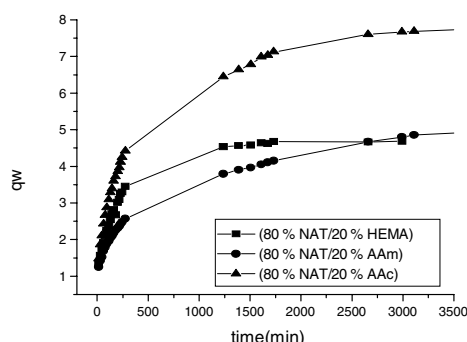
Figure 4: Initial stage (until 3500 min) in typical swelling kinetic curve from poly(NAT-Aac-BIS)2(▲), poly(NAT-HEMA-BIS)2 (■)and poly(NAT-AAm-BIS)2(●)

Water diffusion mechanism analysis in swellable polymeric systems

In contact with water, this last diffuses into the hydrogels swelling them. Diffusion involves the entrance of water into the spaces between hydrogel chains. Equation 2, applied to the initial stages of swelling, was used to determine the type of diffusion of water into hydrogels. For cylindrical shapes, if *n* is in the range of 0.45-0.50, diffusion is Fickian, whereas $0.50 < n < 1.00$ indicates that diffusion is of a non-Fickian type. In Table 1 are listed the values of samples diffusional exponents. In general, the values are over 0.50, so the diffusion of water into the hydrogels had a non-Fickian character (diffusion-relaxation controlled process). This behavior is generally explained as a consequence of a slow relaxation rate of the polymer matrix. The chains need time to respond to swelling pressure and to order themselves for arrange solvent molecules.
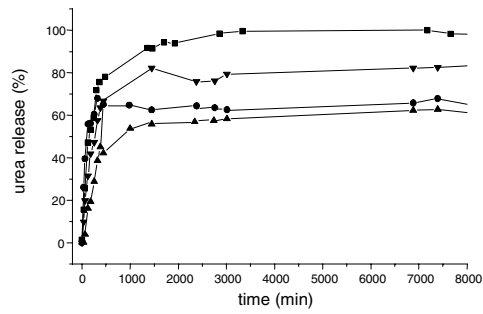
Urea release from hydrogels

Figure 5 shows the urea release from poly (NAT-BIS) 1, poly (NAT-Aam-BIS) 1, poly (NAT-Aac-BIS) 1 and poly (NAT-HEMA-BIS) 1 while Figure 6 shows the urea release from poly (NAT-BIS) 1, poly (NAT-Aam-BIS) 2, poly (NAT-Aac-BIS) 2 and poly (NAT-HEMA-BIS) 2. As can be seen, all hydrogels were able to release urea by a swelling-controlled system but only poly (NAT-BIS) 1 released the total (100 %). Despite this conclusion, it can be noticed that the sequence regarding the release of urea in both cases was poly (NAT-BIS) > poly (NAT-Aam-BIS)1-2 > poly (NAT-Aac-BIS)1-2 > poly (NAT-HEMA-BIS)1-2 products. Table 3 shows the maximum values of urea released from hydrogels in the assays. In most events, the highest values of release were reached past three days approximately. It can be noticed that while higher amounts of NAT were incorporated into the hydrogels, by comparing poly (NAT-BIS)1 and co-monomer-containing products 1-2 in Table 3, a higher urea amount was released. Poly (NAT-BIS) 1 proved to be the best matrix for this purpose since it released the total (100 %) in approximately three days followed by NAT-Aam-BIS-containing products which yielded optimal release values following high swelling values and slow kinetics (Figures 7-8).
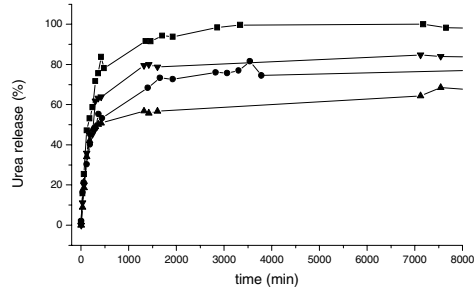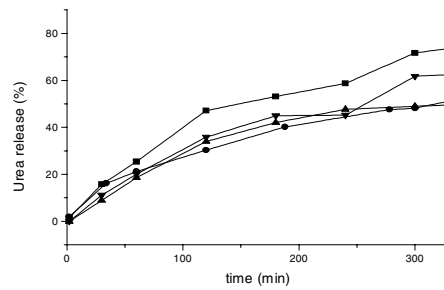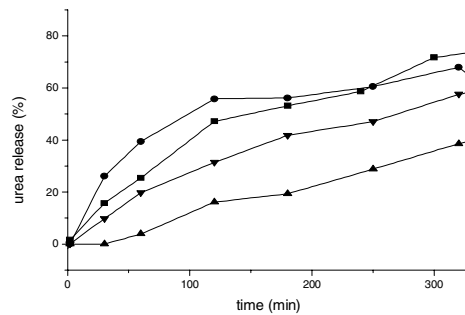
Figure 5: Results of urea release from poly(NAT-BIS)1(■), poly(NAT-Aam-BIS)1(▼), poly(NAT-Aac-BIS)1(●) and poly(NAT-HEMA-BIS)1(▲) until 8000min

Figure 6: Results of urea release from poly(NAT-BIS)1(■), poly(NAT-Aam-BIS)2(▼), poly(NAT-Aac-BIS)2(●) and poly(NAT-HEMA-BIS)2(▲) until 8000min

Figure 7: Results of urea release from poly(NAT-BIS)1(■), poly(NAT-Aam-BIS)1(▼), poly(NAT-Aac-BIS)1(●) and poly(NAT-HEMA-BIS)1(▲) until 300 min

Figure 8: Results of urea release from poly(NAT-BIS)1(■), poly(NAT-Aam-BIS)2(▼), poly(NAT-Aac-BIS)2(●) and poly(NAT-HEMA-BIS)2(▲) until 300 min

Table 3: Maximum value of urea released (%) in aqueous medium from some selected products

Product	Maximum value of urea released (%)
Poly (NAT-BIS) 1	100
Poly (NAT-Aam-BIS) 1	88
Poly (NAT-Aam-BIS) 2	84
Poly (NAT-Aac-BIS) 1	81
Poly (NAT-Aac-BIS) 2	68
Poly (NAT-HEMA-BIS) 1	68
Poly (NAT-HEMA-BIS) 2	63

Conclusions

In this study, free radical polymerization processing was used for the preparation of new gel-like materials derived from NAT monomer varying the crosslinker (BIS or EGDMA), crosslinker concentration, co-monomer (HEMA, Aac or Aam) and initial NAT/co-monomer mole ratio. So, it was confirmed that a rise in the cross-linking agents concentration, resulted in a decrease in both the amount of water retained by the hydrogels (noted in a decrease in q_w) and swelling rate. BIS was chosen as crosslinking agent since it yielded slightly more swellable network structures.

In general, an increase in the amount of Aam incorporated in the copolymers and the minor possibility of crosslinks (by decrease in R), increased the overall matrices hydrophilicity while an increase in HEMA incorporation (involving little variations in R) did not change or decrease the swelling in water. An increase in Aac content from 0 to 20% into the products, results in a rise in q_w although later, an increasing in the carboxyl groups content leads to a decrease in q_w values.

In general, it can be concluded that the incorporation of NAT into the products, enhances the swelling properties in HEMA-BIS-containing hydrogels. On the other hand, the Aam and Aac incorporation and combination into the products improve the swelling properties in NAT-BIS-containing hydrogels.

In diffusion assays, in general, the *n* (number used to determine the type of diffusion) values yielded from all products were over 0.50, so the diffusion of water into the hydrogels had a non-Fickian character.

Regarding urea release (chosen as "model" plant fertilizer agent), it can be concluded that all products were able to release it but poly (NAT-BIS) 1 was the best matrix for this purpose since it released 100 % in three days approximately followed by NAT-Aam-BIS-containing products presenting good release values following high swelling and slow kinetics.

The use of these products in agricultural applications could be important since, once urea (or another bioactive agent) has been released, the hydrogels could be settled in the soil since they have the capacity to hold and retain water serving as reservoir to promote optimal plant growth.

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