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Synthesis and Characterization of Poly (N-Isopropylacrylamide-co-Crotonic Acid) Hydrogels

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Abstract: N-isopropylacrylamide was copolymerized with crotonic acid in order to study the influence of the addition of ionic groups in the water absorbing capacity, the swelling kinetics to 4 and 30ºC, as well as the transition temperature obtained hydrogels. It was found that the addition of the acid groups, slightly increased the water absorbing capacity of the hydrogels, but did not change their transition temperature, however, the water fraction released at the transition point and the decrease in the water release rate were modified. Then the model of the second order kinetics was applied to determiner the process of swelling of the polymers, It was found that, the process was properly described. However when the model of the second order kinetics was applied to predict the behavior of the water release process, finding that this model did not describe the process. The second order model was modified, stating that at time zero samples are at equilibrium swelling, this change in the model was found to describe adequately the process of de-swelling of the hydrogels studied. Increasing the effectiveness for modeling the experimental data, when the acid composition is 10% or greater, with what was obtained a new model to determine adequately the release of water or solutions that could absorb these materials

Keywords: De-Swelling, Crotonic Acid, Hydrogels, Ph –Sensitive

1. Introduction

The ability to absorb water in hydrogels has become a subject of study in recent years. Hydrogels are polymeric networks that swell considerably in the presence of water maintaining their shape until a balance physicochemical [1], on the other hand, the dehydrated state is called xerogel and has a crystalline structure [2]. The hydrophilic of these materials, is due to the presence of various groups such as –OH, -COOH, -$CONH_2$, and -HSO_3 [3]. The properties of hydrogels enable their use in different fields [4-5]. The water absorbing capacity of the hydrogels can be affected by changing some properties of the medium in which these properties are found; such as pH, temperature, ions, solvents etc. [6-9]. Hydrogels have been synthesized by various methods, trying to increase their ability to absorb water, which depends on the type of polymer and the synthesis conditions [10]. In this context materials that respond to changes in the temperature of the system have been found [9-10]. The transition temperature of hydrogels of N-isopropylacrylamide (polyNIPA) is an important property in the study and application of materials prepared with this monomer. The volume phase transition temperature (T_{TVP}), which is characterized by a sudden decrease in the capacity to absorb water, and occurs at around 32ºC [11-13]. These transitions, which occur when changing the temperature or composition of solvent, have been observed in various types of hydrogels [14-17]. The polyNIPA has its T_{TVP} around 32°C [18]. Different studies have found that the copolymerization of hydrophilic monomers with NIPA modifies both the water absorbing capacity as well as the transition temperature [19-

20], both linear polymers and polymer gels. The ability to absorb water can be modified by adding co-monomers containing ionic groups or increasing the water release rate at the point of transition by adding various ionizable co-monomers. It has been reported that the flexibility of the chains in the polymer matrix can be modified by the variation of the proportion of solvent in the initial reaction mixture [20], increasing the proportion of solvent in the initial reaction mixture, increases the flexibility of chains and thus increases the porosity of the network when swollen, increasing the gaps and allowing more water not associated within the polymer matrix to enter it, whereby the water fraction released in the transition point is unchanged. It has been found that the water absorbing capacity of hydrogels derived from acrylamide increases, when acrylic acid is added as co-monomer (CH_2=CHCOOH having a pKa of 4.26 at 25ºC) [21-24], on the other hand, studies have shown that the addition of carboxylic groups to PolyNIPA hydrogels, besides increasing the ability to absorb water, also modify the transition temperature (T_{TVP}) [25], so that the addition of an acid, such as crotonic acid (CR) CH_3CHCH = COOH (pKa = 4.69 at 25ºC), must have a greater influence on the ability to absorb water, due to the large number of methyl groups present hence decreasing the hydrogels hydrophilic behavior, similarly as to how primary alcohols increase the length of the carbon chain thus decreasing its solubility in water. Adding a monomer such as CR would provide groups to the ionic polymer network, enabling this material to both absorb different substances with polar charge and substances that produce ions in aqueous solutions, which may further modulate the release of water at the transition points.

To determine if the second order kinetic model (equation 1) can be applied to determine the behavior in the swelling process, and in the deswelling process for NIPA / AC hydrogels. In the present paper NIPA is co-polymerized in various proportions with crotonic acid, yielding polymer gels, which showed different water release rates when placed in distilled water at 30°C. When samples reached equilibrium swelling, the medium temperature was increased to 40ºC, and was found that hydrogels containing the highest proportion of CR, have a lower rate of release of water. The second order model (model 1) was used to obtain the kinetic parameters of the synthesized hydrogels, finding an adequate description of the process of swelling them. When applying the model of second order kinetics to the process of deflation of the samples, it was found that the model did not describe this behavior. Exist large deviations of the experimental data with respect to the data obtained with the second order model, so a new model for the kinetic of deflation of the hydrogens was proposed, with this new model (model 2) could be described in a way satisfactory the kinetics of deflation of the polymer studied and the kinetic parameters of this model were obtained

2. Materials

N-isopropylacrylamide (NIPA), with a purity of 99%; potassium persulfate (KPS) used as initiator, with a purity of 99%; N, N, N, N-tetramethyl-ethylenediamine (TMEDA) used as accelerator, and N.N-methylenebisacrylamide (NMBA) used as crosslinker agent, with a purity of 99%, they were purchased from TCI, crotonic acid (CR) 98% purity from Aldrich, bi-distilled water (products Selectropura) were used as received.

2.1. Synthesis of Hydrogels

Hydrogels were prepared by radical copolymerization of NIPA and CR at 4ºC in cylindrical glass tubes, adding 1, 2 and 3% by weight of crosslinking agent, initiator, and accelerator respectively, with respect to the total monomers, and allowing them to react for 24 hours at 4°C. The proportion of 90/10 water/monomer in weight was used in all cases. The proportions of the co-monomers were varied to obtain different hydrophilic properties. After reacting, the hydrogels were removed from the test tubes and cut into cylinders, the samples were placed in distilled water for 7 days to allow for the material not added to the network can be eliminated, then letting them stand at dry room temperature for two days (to avoid breaking the material by a sudden drying) and then moved to a vacuum oven until constant weight.

2.2. Swelling Kinetics

To determine the swelling kinetics, the dried samples were weighted and placed in water at 4°C and at different times, samples were removed from the medium, drying the surface with absorbent paper and weighed. The difference between the dry sample weight and the weight of the swollen sample at various times, the swelling kinetics (this process was repeated at 30°C) is determined. The swelling degree (H) is defined as:

$$H = \frac{Wet\ Weigth - Dry\ Weigth}{Dry\ Weigth} = \frac{ph - ps}{ps} \quad (1)$$

To describe the kinetics of swelling of hydrogels has been used the second order model, which is commonly used to describe the swelling behavior [26-28]. Considering second-order kinetics, the rate of swelling at any given time is directly proportional to the available swelling capacity before reaching the maximum or equilibrium uptake, W_∞. This remaining swelling capacity is defined as W_∞ - W, where W is the swelling or solvent uptake at time t and K is the proportionality constant between the rate of swelling and the unrealized swelling capacity. This model has the following form (model 1):

$$\frac{dW}{dt} = K(W_\infty - W)^2 \quad (2)$$

Where:

$$W = \frac{Wet\ Weigth - Dry\ Weigth}{Wet\ Weigth} = \frac{ph - ps}{ph} \quad (3)$$

Which when integrated and evaluated with W = 0 when t = 0 is obtained:

$$W = \frac{KW_{\infty}^2 t}{1 + KW_{\infty} t} \tag{4}$$

Combining equations (1) and (3) we obtain:

$$W = \frac{H}{H+1} \tag{5}$$

$$W_{\infty} = \frac{H_{\infty}}{H_{\infty}+1} \tag{6}$$

Combining equations (5) and (6) replacing in the equation 4 we obtain:

$$\frac{t(H+1)}{H} = \frac{(H_{\infty}+1)^2}{KH_{\infty}^2} + \frac{H_{\infty}+1}{H_{\infty}} t \tag{7}$$

By plotting t (H + 1) / H vs. time where a straight line we obtain:

Slope is:

$$m = \frac{H_{\infty}+1}{H_{\infty}} \tag{8}$$

The intersection is:

$$b = \frac{(H_{\infty}+1)^2}{KH_{\infty}^2} \tag{9}$$

And the value of K can be calculated:

$$K = \frac{(H_{\infty}+1)^2}{bH_{\infty}^2} \tag{10}$$

Rearranging equation (7) yields:

$$H = \frac{t}{t(m-1)+b} \tag{11}$$

With which the swelling is obtained as a function of time

2.3. Swelling at Equilibrium with Respect to Temperature

Equilibrium swelling was determined for the temperature from 4 up to 46°C. The transition temperature (T_{TPV}) is located at the point where the water absorbing capacity decreases abruptly.

2.4. Water Release Rate

Dried samples (xerogel) were weighted and placed in distilled water at 30°C, when they reach equilibrium swelling, medium temperature is raised to 40ºC and the process of de-swelling is measured by weighing the samples every certain time as described above. Now can be consider the rate of de-swelling at any given time is directly proportional to the available swelling capacity W. To model the process of de-swelling Model 1 is amended as:

$$\frac{dW}{dt} = -KW^2 \tag{12}$$

And integrating it within the limits (T, W) in (0, W_{∞}) to (T, W), we obtain:

$$\frac{1}{W} = \frac{1}{W_{\infty}} + Kt \tag{13}$$

by using equations 5 y 6 and replacing in the equation 13 is obtained:

$$\frac{(H+1)}{H} = \frac{H_{\infty}+1}{H_{\infty}} + Kt \tag{14}$$

where you can get:

$$\frac{(H+1)}{H} = Kt + c \tag{15}$$

Rearranging we get:

$$H = \frac{1}{Kt + c - 1} \tag{16}$$

Obtaining equation that describes the behavior of the process of de-swelling (Model 2) is obtained.

3. Results

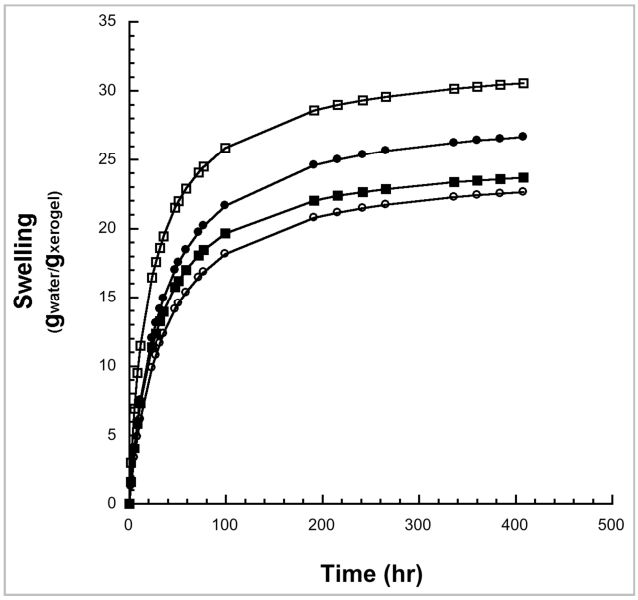

Figure 1. *Swelling kinetics at 4°C for hydrogels as a function of the mass ratio of NIPA/CR 100/0 (◯), 95/5 (■), 90/10 (□) and 85/15 (●).*

In Figure 1 it can be seen that the addition of CR to hydrogels polyNIPA, increase their ability to absorb water,

this is caused by the addition of carboxylic groups to the network, which has been reported in previous studies [29-30], although it was expected that the addition of the carboxylic groups, had a greater influence on the ability to absorb water, the presence of the methyl group located after the double bond, increased hydrophobic interactions of the protonic acid, which balances the influence of the group carboxylic acid group in the hydrophilic behavior, whereby the water absorbing capacity is only slightly increased. Table 1 shows the kinetic data of hydrogels synthesized at 4°C. But when the composition of CR reached 15%, a small decrease in the ability to absorb water it can be observed, it has been observed that the ability to absorb water polyNIPA hydrogels, increases with decreasing temperature [31], so the addition of CR at 4ºC provides him a small increase in their ability to absorb water, however this influence on the increase is limited by the hydrophobic part of the molecule CR and an excess of acid will bring this decrease in the ability to absorb water. (To determine the addition of CR to the network, 1 gram of xerogel was placed in 50 ml of distilled water at 25°C, allowing the samples to reach equilibrium, the hydrogels were destroyed and placed under constant stirring, to subsequently determine the pH, these values are presented in Table 2) where it can be observed that the higher CR content in the sample increases the pH of the resulting solution. However, the water absorbing capacity of hydrogels with carboxylic groups is always greater than the water absorbing capacity of hydrogels polyNIPA. When the data obtained at 30ºC (Table 2) is reviewed, it can be seen that in all cases the water absorbing capacity is increased due to the addition of the carboxylic groups, but when the capacity to absorb water compared hydrogels at 30ºC, with respect to the water absorbing capacity of hydrogels at 4ºC, it can be seen that there is a decrease in this capacity, this is because the NIPA is a thermosensitive monomer and its ability to absorb water gradually decreases with increasing temperature, when the temperature is below 32ºC [32], which explains the decrease of NIPA hydrophilic behavior and thus swelling of hydrogels.

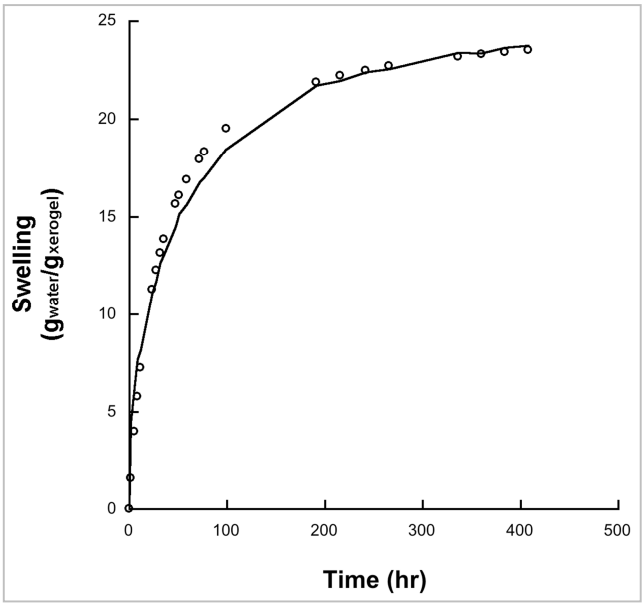

Figure 2. *Kinetics of swelling for NIPA hydrogel at 4ºC, experimental data (○) and mathematical model 1 (-) for the hydrogel with proportion of NIPA/CR of 85/15.*

Table 1. *Kinetic parameters of hydrogels, obtained at 4ºC, calculated with Model 1.*

NIPA/CR % weight	100/0	97/3	95/5	90/10	85/15
m (slope)	1.041	1.0318	1.0347	1.0307	1.0394
b (intersection)	88.60	59.30	69.35	42.13	68.74
Hteorical (gwater/gxerogel)	24.65	31.49	28.83	32.57	25.38
K ghydrogel/(gwater-min)	0.0128	0.0203	0.0156	0.0315	0.0159
R2	0.9999	0.9999	0.9999	0.9999	0.9999
Hexperimental(gwater/gxerogel)	22.83	29.62	26.62	31.02	23.56
Standard deviation	0.8	0.9	0.6	0.7	0.9

Table 2. *Kinetic parameters of hydrogels, obtained at 30°C, calculated with Model 1.*

NIPA/CR % weight	100/0	97/3	95/5	90/10	85/15
m (slope)	1.098	1.0722	1.0757	1.0721	1.0692
b (intersection)	125.98	134.50	163.15	88.52	145.18
Hteorical(gwater/gxerogel)	10.2112	13.86	13.21	13.87	14.46
K ghydrogel/(gwater-min)	0.0062	0.0083	0.0062	0.0110	0.0077
R2	0.9999	0.9999	0.9999	1.0000	0.9999
Hexperimental(gwater/gxerogel)	9.5122	12.53	11.88	12.99	12.59
Standard deviation	0.50	0.97	0.44	0.62	0.81
pH	7.90	6.27	5.82	4.68	4.23

The solid lines in Figure 2 are model predictions swelling of second order. It can be seen that Model 1 predictions are a good approximation to the experimental swelling behavior of the hydrogels synthesized (symbols). This is corroborated with the kinetic data presented in Table 1, where one can observe that the correlation coefficient for all samples is close to 1, also the average swelling obtained with experimental data and standard deviation less is presented to 8%, and predicts adequately the experimental swelling ($H_{\infty real}$), that can compare with the theoretical equilibrium swelling ($H_{\infty teorical}$).

Figure 3 shows the equilibrium swelling normalized to the temperature of 4°C, as a function of temperature, where it can be seen that the addition of CR does not change the transition temperature of phase volume, which is presented between 32

and 34°C, however the fraction of water that is released into the transition point, if it is affected by the increase in CR composition. This modification shows the influence of the methyl group of CR, increasing the hydrophobic behavior of the synthesized copolymer. This sharp decline in the water absorbing capacity of the hydrogels increased can be used for the absorption of active substances or (pollutants) metal ions at temperatures below the transition point and subsequent release or recovery temperatures above this transition temperature or transition temperature thereof depending on the hydrogel composition and its absorption capacity.

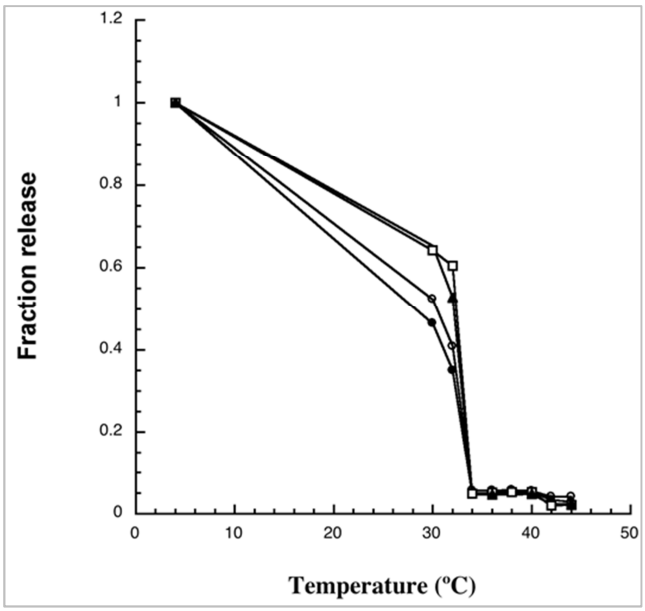

Figure 3. *Swellings in the standardized at 4ºC with respect to temperature equilibrium, the transition temperature of phase volume, depending on the mass ratio of NIPA/AC 100/0 (●), 95/5 (○), 90/10 (□) and 85/15 (▲).*

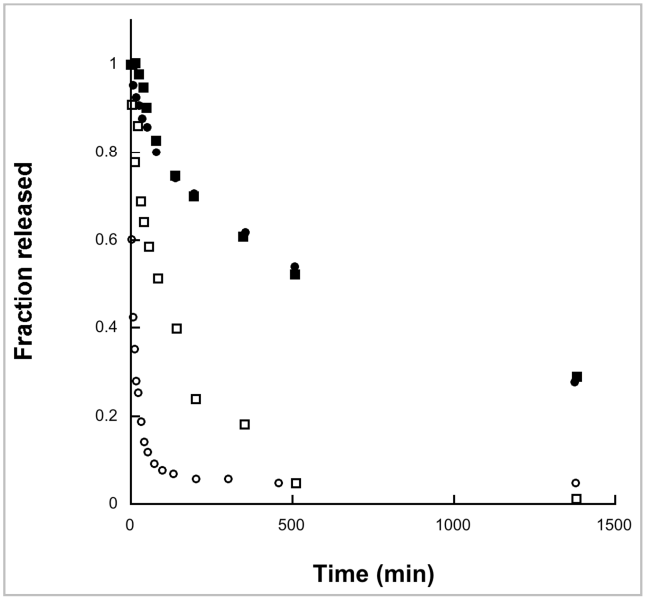

Figure 4. *Fraction of water released depending on the proportion of NIPA/CR 100/0 (○), 95/5 (□), 90/10 (●) and 85/15 (■).*

Hydrogels are placed to swell at 30ºC and when they reach the equilibrium swelling, the temperature rises to 40ºC, the weight of samples at different times de-swelling kinetics is obtained. It was found that the rate of release of water decreases with increasing CR composition in the samples. As mentioned earlier, the presence of carboxylic groups increases the hydrophilic behavior of the copolymers, increasing the polymer-solvent interaction that retards the diffusion of water into the environment. Thereby it can be modulated dosage of the active substances contained in the gel and released at a particular concentration. When the model 1 is applied to predict the process of de-swelling of hydrogels polyNIPA, it appears that in the early days the model is unable to predict the behavior of the process, even negative values are generated and is only able to model de-swelling of hydrogels, until values are achieved above 60% (solid line figure 5). Furthermore the model 1 predicts adequately the process of de-swelling polyNIPA and the final equilibrium swelling hydrogels ($H_{0teorical}$) for all studied (Table 3). The elastic factors are those that govern the process of de-swelling of polyNIPA, when this is placed at temperatures above the transition point (Ttpv), whereby the model of second order kinetics may not fit the experimental data. The CR joined the network, increases interactions with the water causing the water release process is governed by the diffusion so model 2 is able to predict the behavior of polymer. Both models presented in this study correspond to a second order kinetic although in model 1 when time is 0 then W = 0 while in model 2 when time is 0 then W = equilibrium.

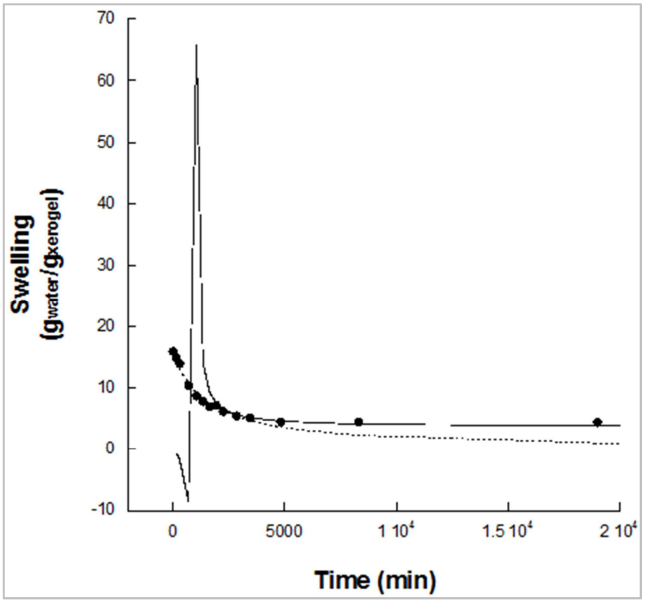

Figure 5. *Mathematical model to describe the kinetics of the hydrogel polyNIPA deswelling, model 1 (-), model 2 (-------) experimental data (•).*

So as CR concentration increases model 2, begins to better adjust the de-swelling process hydrogels (NIPA/CR 95/5) figure 6, since the addition of CR, slows the process of de-swelling, causing the solvent diffusion process has greater

influence than the elastic processes due to shrinkage of the polyNIPA, similar results have been observed in poly(N, N-dimethylacrylamide-co-NIPA) [33]. This can be seen in the Figures 7 and 8 where present hydrogels containing 10 and 15% of CR. In all cases, the model 2 can adequately predict the maximum equilibrium swelling ($H_{\infty teorical}$) reached by the samples, but only approaches the value of the swelling minimum ($H_{0teorical}$) balance achieved during de-swelling of the samples, as shown in Table 4.

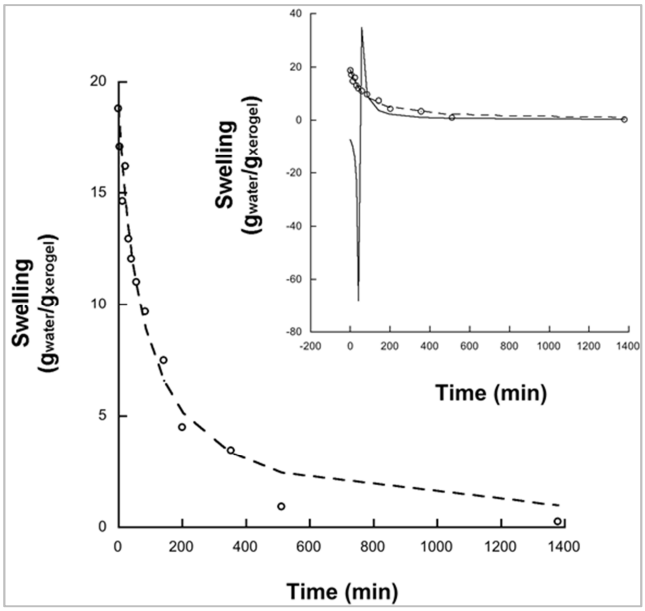

Figure 6. *Mathematical models describing the kinetics of swelling of the hydrogel NIPA/CR studied 95/5, Model 1 (solid line), model 2 (- - -), experimental data (o).*

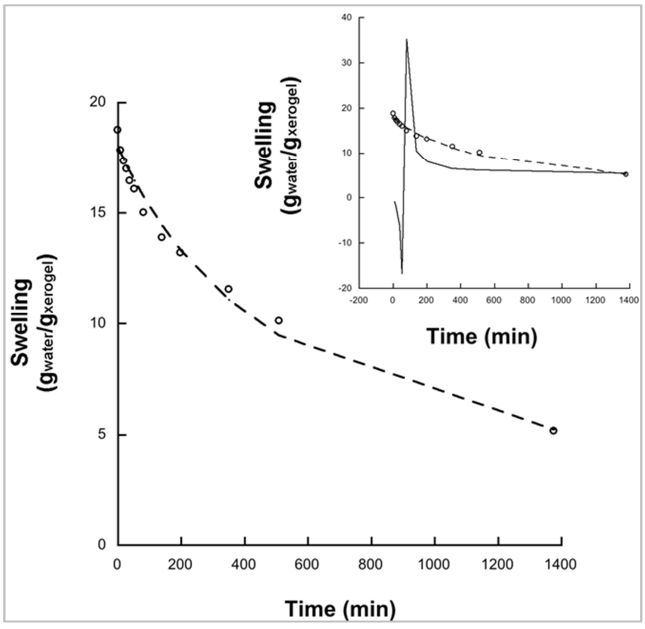

Figure 7. *Mathematical models describing the kinetics of de-swelling for the hydrogel (NIPA / CR) 90/10 Model 1 (solid line), model 2 (- - -), experimental data (o).*

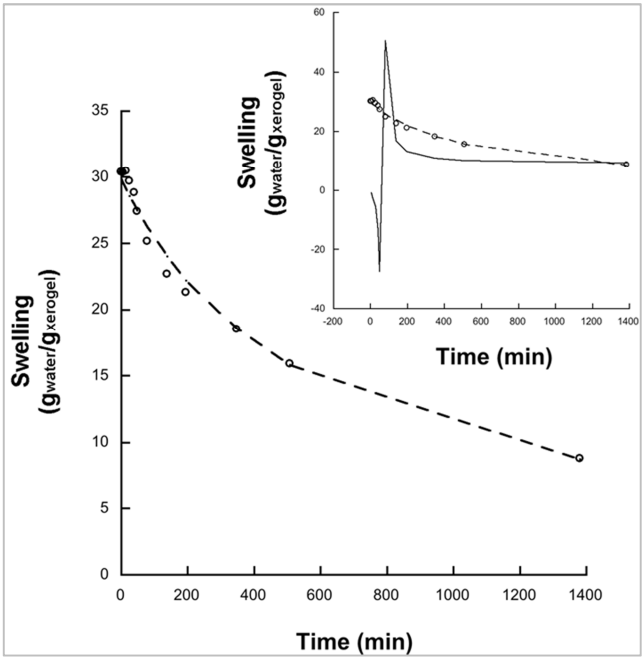

Figure 8. *Mathematical models describing the kinetics of swelling of the hydrogel NIPA / CR 85/15 examined, Model 1 (solid line), model 2 (- - -), experimental data (o).*

Table 3. *Data obtained kinetic model 1, for de-swelling, when the gels reached equilibrium swelling at 30 ° C and then are placed at 40°C.*

NIPA/CR % weight	95/5	90/10	85/15
Hexperimental (gwater/gxerogel)	0.240	5.172	8.791
m (slope)	4.981	1.189	1.112
Standard deviation	0.1234	0.1256	0.1456
b (Intersection)	-24086	-790	-436
Hteorical (gwater/gxerogel)	0.251	5.280	8.952

Table 4. *Kinetic data obtained with the model 2, for de-swelling, when the gels reached equilibrium swelling at 30°C and then are placed at 40°C. The initial swelling ($H_{0teorical}$) and swelling at equilibrium ($H_{\infty teorical}$) is presented, which were calculated with model 2.*

NIPA/CR %weight	95/5	90/10	85/15
m (slope) (*106)	0.1161	1.775	1.090
H∞teorical(gwater/gxerogel)	18.945	20.392	30.307
c (intersection)	1.053	1.049	1.033
H∞experimental(gwater/gxerogel)	18.783	21.543	30.381
Standard deviation	1.2466	1.6678	1.988
R2	0.988	0.995	0.985
H0teorical(gwater/gxerogel)	0.986	5.111	8.108
H0experimental(gwater/gxerogel)	0.240	3.665	8.791

4. Conclusions

In this paper hydrogels Poly (NIPA-co-CR) were synthesized by varying the composition of acid, it was observed that the addition of CR slightly increased the water absorbing capacity of hydrogels and although not change the temperature transition of polyNIPA, if increased water fraction released in the transition temperature with increasing acid composition in the polymer, the swelling kinetics of hydrogels and kinetics de-swelling was determined and found to model second order must be modified to a good interpretation of the experimental data. The second order

model was modified and was found to adequately describe the process of de-swelling of hydrogels, improving the description, as CR content in the samples increased.

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