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Polymer 43 (2002) 63–70

polymer

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Kinetics of water absorbency in AA/AMPS copolymers: applications of a diffusion–relaxation model

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Received 23 April 2001; received in revised form 31 July 2001; accepted 14 August 2001

Abstract

Superabsorbent copolymers, based on acrylamide, 2-acrylamido-2-methyl-propanosulfonic acid and a divinyl crosslinker, *N*,*N*′-methylenebisacrylamide, have been synthesized by free radical solution and inverse emulsion polymerization. The copolymerization has been carried at different pH values of the monomer mix reaction medium.

The copolymers were characterized by their dynamic swelling behavior in deionized water, i.e. the mass of water absorbed by a sample of copolymer was measured vs time. The results were analyzed in terms of the Berens–Hopfenberg non-Fickian equation, leading to a one-only-term relaxation. These kinetics were interpreted by the diffusion–relaxation model and offer quantitative information by diffusivity at 20°C of water in the copolymers. In this investigation, the results have been confirmed within experimental error as the sample of the copolymer is swollen. © 2001 Published by Elsevier Science Ltd.

Keywords: Swelling; Superabsorbent copolymers; Absorption kinetics

1. Introduction

Water absorptivity by a polymer, leading to an increased volume and mass — its swelling — is an important property in applications, and has been studied by many researchers on the so-called superabsorbent polymers [1]. The objective in manufacturing them is to have high absorption ratios and efficiencies. Thus, swellings of the order of at least hundreds of times the initial mass have been obtained [2]. Several studies have been made focusing useful applications [3], such as in agriculture — for the maintenance of soil humidity [4] and the controlled release of agrochemicals [5]; and in pharmaceutics and biomedicine [6,7] — for the biological retention of fluids and the controlled drug release [8,9].

The copolymers studied were synthesized from the monomers acrylamide (abbreviated as AA), 2-acrylamido-2-methyl-propano-sulfonic acid (abbreviated as AMPS), and bisacrylamide (abbreviated as BA). The copolymers synthesized were AA/AMPS and AA/AMPS/BA, with the bifunctionality of BA introduced in order to try to improve the swelling capacity. These monomers were chosen due to the following reasons: AA is a rather cheap, common monomer, and AMPS is compatible with water, as a resulting anionic polymer was sought. Also, regarding BA, in order to enhance the crosslinking, further copolymers were prepared with this monomer as a crosslink agent.

In the application of superabsorbents, it is important to know the kinetics of the absorption process. Several mechanisms for the kinetics of the diffusion process have been proposed, from the simplest, Fickian diffusion [10,11] to other, more complex ones, of the viscoelastic kind [12], namely with relaxation contributions [13]. The models for the former and the latter mechanisms have been presented, respectively, under the designations of Fickian and non-Fickian diffusion.

With regard to the kinetics of the diffusion process leading to the swelling of polymers, the following steps are usually considered [14]: diffusion of the water molecules in the structure of the polymer, and relaxation of the chains of the hydrated polymer, with the expansion of the structure of the polymer in the water around it. The swelling behavior varies according to which step becomes decisive in the mechanism of the process, thus determining the model which best fits the behavior under observation.

In cases where the classical, Fickian diffusion applies, the system is controlled by the diffusion step, as the solvent mobility is very low in comparison to the relaxation rate

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0032-3861/02/$ - see front matter © 2001 Published by Elsevier Science Ltd.
PII: S0032-3861(01)00596-1

Nomenclature

D	diffusivity, m^2/s
d	particle diameter, m
i_R	number of relaxation terms
k_1	relaxation rate constant, s^{-1}
k_F	diffusion rate constant, s^{-1}
M_t	mass of absorbed water, as a function of time, t, g
n	transport mode related exponent
r	mass of absorbed water per unit mass of dry polymer sample, g/g
t	time, s
w	fraction of the mass of absorbed water in relation to its final value
x	weight of diffusion in the absorption [with $(1-x)$ the weight of relaxation]
η	advancement of absorption $(0 \leq \eta < 1)$
Indices	
F	index for Fickian diffusion
infl.	inflection point
R	index for relaxation

of the polymer. In the non-Fickian processes, the diffusion and relaxation rates may be comparable.

In Fickian diffusion, the absorbed mass, $M_{t,F}$, per unit mass of the polymer sample at time t is expressed by the classical equation for spheres [15]

$$M_{t,F} = M_{\infty,F}\left[1 - \frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\exp(-n^2 k_F t)\right]$$

where $M_{\infty,F}$ is the final, equilibrium amount sorption in the diffusion process and $k_F = 4\pi^2 D/d^2$ is the diffusion rate constant (inverse of time) for a diameter d (i.e. an equivalent diameter, to weight some non-sphericity). From the auxiliary parameter k_F, the diffusivity, D, can be obtained.

The determination of the particle size was made by the laser light-scattering technique, as described in Section 2. Regarding shape, the observation of the particles led us to approximate them by spheres, which is coherent with the usual assumption.

A simple model [16] to elucidate the transport mode for the absorption of water in hydrophilic polymers is $M_t/M_\infty = kt^n$, with M_t the water uptake, M_∞ its final (equilibrium) value, k a constant characteristic of the system, n an exponent (obtainable by simple regression) characteristic of the transport mode, and t the diffusion time. A typical value of n is 0.5 for purely Fickian processes [16], which mathematically agrees with the behavior of the Fickian equation for small times.

As to non-Fickian absorption, a useful model results from the further inclusion of relaxation. Namely, the diffusion of small molecules in a polymer is complex, not adhering satisfactorily to the Fickian model. The deviations from the Fickian behavior can be attributed to the relaxation phenomenon. A model of diffusion–relaxation was proposed by Berens et al. [13] considering a linear superposition of both contributions. Thus, the mass corresponding to relaxation, $M_{t,R}$, per unit mass of the polymer sample at time t, may be expressed by

$$M_{t,R} = \sum_{i=1}^{i_R} M_{\infty,i}[1 - \exp(-k_i t)]$$

where $M_{\infty,i}$ is the final, equilibrium amount sorption in the relaxed process, and k_i is the relaxation rate constant (inverse of time). The total mass, M_t, absorbed per unit mass of the polymer sample at time t, will be expressed as $M_t = M_{t,F} + M_{t,R}$. In the above assumption, we later inferred that a single term, i.e. $i_R = 1$, turned out to be in accordance with the data in the cases under observation.

In the model presented here, the behavior of absorption was explained both in terms of the diffusion of the penetrant in a direction of the polymer network, and in terms of the relaxation process in the network. The absorption was thus expressed by a non-Fickian equation, containing an expression of Fickian transport (the first term of the above equation) and a relaxation expression (the second term). The diffusion is led by a gradient related to the equilibrium concentration, and the relaxation, whose terms do not depend on the particle size, is related to the dissipation of the swelling tension, this tension being induced by the admission of the molecules of the penetrant.

In order to apply the model equation, a computer program and a spreadsheet were developed. The optimal parameters were thus determined for all the synthesized copolymers. The program was based on the minimization (through the Nelder and Mead sequential simplex [17]) of residues between experimental and calculated absorption values.

2. Experimental

The polymer syntheses were performed by two different copolymerization processes, solution and inverse emulsion, and under various pH values at constant temperature, and the polymers obtained were studied regarding their kinetic swelling ability.

2.1. Synthesis of the copolymers

A set of copolymerizations of AA with cationic monomer AMPS and BA as the crosslinking monomer were programmed in order to determine the dynamic of the water uptake of the resulting copolymers (including those of Ref. [18]). The monomers AA and BA were supplied by Resiquímica, SA (Sintra, Portugal) and the monomer AMPS by Lubrizol Corporation (USA).

Free radical solution and reverse microemulsion were the polymerization processes used for the synthesis of the superabsorbent copolymers. The polymerization was always carried in a reactor equipped with a stirrer, a reflux condenser, a thermometer, a dropping funnel and a gas inlet tube.

In free radical solution copolymerization, the monomers AA [itself a 50% (w/w) solution] and AMPS in a molar ratio of 70:30 were dissolved in distilled water, and this aqueous phase was placed in the reactor. Also, the monomers mentioned with BA in a molar ratio of 69.5:30:0.5 were treated by free radical solution.

In the reverse microemulsion process, an aqueous monomer solution is dispersed in an organic phase. Regarding the organic phase, it was prepared by weighing the appropriate amount of Isopar M and Tween 85, and by introducing the organic phase in the glass reactor with continuous stirring. The monomer mix was then added to the organic phase emulsifier. The pH value of the monomer solution was adjusted by the addition of aqueous sodium hydroxide (from Fisher Chemicals).

Nitrogen was bubbled into the mixture at a slow rate for 3 h, while permanently stirring, and heated to 50°C, after which the initiation solution of potassium persulfate (from Merck) in distilled water was added in the top of the reactor. The reacting solution was then polymerized at 50°C for a further 5 h in nitrogen flow. After cooling to room temperature, the copolymer was isolated through precipitation of the product by mixing the solution with acetone. Finally the copolymer was dried in an oven at 60°C.

2.2. Determination of particle size

The determination of the particle size by the laser light-scattering technique was made on a Malvern Master Sizer X, an apparatus, that is composed by an optical device and the appropriate software to calculate a mean diameter. The particles, as regard to shape, were considered spheres, and the Sauter mean diameter was the representative parameter.

The sample was dispersed in *n*-heptane, as this dispersant does not interact with the polymer sample, namely regarding the swelling behavior, and, being an optically clear liquid, also does not affect the measurement procedure. The cell system comprises an ultrasonic tank for sample preparation, stirring facilities to keep samples suspended, and a pump to circulate the sample to the measurement cell.

The Sauter mean diameter for the sample was 18 μm, which was subsequently considered in the absorption kinetics.

2.3. Measurement of the kinetics of swelling

In order to determine the kinetics of swelling of the AA/AMPS and AA/AMPS/BA specimens, measurements of absorbency were measured in deionized water at 20°C as a function of time.

The procedure used for following the sorption kinetics experiments was to place weighed samples of dry polymer in a glass with an excess of deionized water, the glass being immersed in a thermostat bath controlled within 0.01°C.

The water absorbed by the copolymer for certain specified periods of time was obtained by removing the sample from the water bath and blotting excess water from the sample; weighing the sample; and replacing it in water for further swelling. The trials were repeated until the water content equilibrium was attained, defining the maximum value of water uptake.

The observed water retention or increment, r, was expressed as mass of water absorbed per unit mass of the dry polymer sample, $r = m(H_2O)/m(\text{dry polymer})$, and the mass of absorbed water is thus measured at each instant as $m(H_2O) = m(\text{wet polymer}) - m(\text{dry polymer})$. The weight fraction, w, is the fraction of the mass of absorbed water in relation to its final value, r_∞, i.e. $w = r/r_\infty$.

The method used to obtain the kinetics of swelling presents some practical difficulties because the sample of the copolymer has to be removed from the swelling liquid in order to make a weighing of the copolymer after blotting the excess water from the surface of the sample. So, in order to reduce the experimental error, the swelling measurements were performed in triplicate. It was observed that the range of the values did not exceed about 5% (with most values in the interval 2–3%) of the smallest one. The averages of each set of three values (for the same instant of the various experiments) are, thus, the ones considered to calculate the fractional penetrant uptake.

The kinetics of swelling is summarized in Table 1 for three representative samples of AA/AMPS copolymers with a molar ratio 70:30 synthesized by the solution method at different pH values of reaction medium. In this table and the following ones, t is the diffusion time, with r and w already defined.

The effect of the crosslinking monomer BA and the method of polymerization in the kinetics of swelling have also been examined. Table 2 contains the results of the kinetics measurements of the copolymers AA/AMPS/BA synthesized in solution, and Table 3 shows corresponding copolymers synthesized in reverse emulsion.

The swelling kinetics as well as the final swelling capacity also depends on other conditions of polymerization, namely the pH of the aqueous phase. In all the cases, the swelling behavior is faster and larger at higher pH values (e.g. 10) and this fact is easy to interpret. At pH 10, most of the sulfonic acid groups are in the form of sulfonate and this leads to a higher ionic strength of the aqueous medium. At this higher ionic strength, the negatively charged ionic backbone of the polymer is more expanded and therefore, at later stages, this expanded form makes the water molecules penetration easier. On the contrary, at lower pH (such as 4), the sulfonic acid groups are mostly in a protonated form, and the organic part of the solution is somewhat segregated (which can be observed by the turbidity) and these segregated domains have a less polar character and therefore, result in a polymer with lower water compatibility. The polymers formed at lower pH have thus a less expanded, or even globular, structure, and this type of structure makes the

Table 1
Kinetics of swelling of poly-(AA-*co*-AMPS), 70:30, in water: solution copolymerizations (*t*, time (min); *r*, water increment [$m(H_2O)/m$(dry polymer)]; *w*, weight fraction)

Sample C-1, pH = 0.16			Sample C-2, pH = 1.1			Sample C-3, pH = 3		
t	*r*	*w*	*t*	*r*	*w*	*t*	*r*	*w*
0	0	0	0	0	0	0	0	0
2	79	0.118	2	208	0.496	2	228	0.578
4	196	0.294	4	309	0.736	4	294	0.744
6	331	0.495	6	354	0.842	6	370	0.936
8	443	0.663	8	373	0.890	8	395	1
10	535	0.800	10	384	0.914			
12	605	0.906	12	398	0.947			
14	653	0.977	14	413	0.983			
16	669	1	16	420	1			

water penetration more difficult. Furthermore, it is well known that globular forms or nodules in polymers have a reduced swelling capacity due to mechanical limitations to the movement of the individual molecules as well as a lower intrinsic affinity of water to the globule macromolecular structure.

As will be seen, the dynamic swelling profile was found to be a characteristic of each copolymer and was a means to describe the water diffusion mechanism in the copolymers.

3. Model and results

In order to quantitatively describe the water diffusion in the copolymers synthesized, it is necessary to find an appropriate model, the cited Berens–Hopfbenberg having been adopted. After the application of the proposed model, several results of diffusivity and relaxation were obtained, leading to the acceptance of the model.

3.1. The diffusion–relaxation model

As stated, the model for the kinetic behavior derives from the simultaneous consideration of the Fickian and relaxation terms. The equation thus becomes

$$M_t = M_{\infty,\mathrm{F}}\left[1 - \frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\exp(-n^2 k_{\mathrm{F}} t)\right] + \sum_{i=1}^{i_{\mathrm{R}}} M_{\infty,i}[1 - \exp(-k_i t)]$$

The application of this equation to the synthesized polymers led to the simpler consideration of only one relaxation term — i.e. $i_{\mathrm{R}} = 1$ —, as mentioned and will be detailed later, upon the analysis of the data. Dividing by M_∞, the equation becomes

$$\frac{M_t}{M_\infty} = \frac{M_{\infty,\mathrm{F}}}{M_\infty}\left[1 - \frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\exp(-n^2 k_{\mathrm{F}} t)\right] + \frac{M_{\infty,\mathrm{R}}}{M_\infty}[1 - \exp(-k_{\mathrm{R}} t)]$$

Table 2
Kinetics of swelling of poly-(AA–AMPS–BA), 69.5:30:0.5, in water: solution copolymerization (*t*, time (min); *r*, water increment [$m(H_2O)/m$(dry polymer)]; *w*, weight fraction)

Sample C-4, pH = 4			Sample C-5, pH = 10		
t	*r*	*w*	*t*	*r*	*w*
0	0	0	0	0	0
1	61	0.426	2	233	0.500
2	87	0.607	4	328	0.704
4	114	0.796	6	376	0.806
6	126	0.874	8	396	0.848
8	135	0.942	10	428	0.919
10	144	1	12	437	0.936
			14	446	0.957
			16	450	0.966
			18	453	0.972
			20	466	1

The terms between brackets, notated below by η_{F} and η_{R},

Table 3
Kinetics of swelling of poly-(AA–AMPS–BA), 69.5:30:0.5, in water: inverse emulsion copolymerizations (*t*, time (min); *r*, water increment [$m(H_2O)/m$(dry polymer)]; *w*, weight fraction)

Sample C-6, pH = 7			Sample C-7, pH = 10		
t	*r*	*w*	*t*	*r*	*w*
0	0	0	0	0	0
1	102	0.310	1	218	0.2540
2	198	0.601	2	666	0.7778
3	261	0.793	3	731	0.8529
4	287	0.873	4	752	0.8772
5	309	0.938	5	803	0.9373
6	315	0.958	6	837	0.9768
7	320	0.973	7	857	1
8	323	0.980			
10	323	0.980			
12	328	0.996			
14	329	1			

refer to the Fickian and relaxation contributions, respectively, and their coefficients, x and $1 - x$, represent the weights of the contributions, leading to

$$\frac{M_t}{M_\infty} = x\eta_F(t;k_F) + (1 - x)\eta_R(t;k_R)$$

where we have made explicit the parameters k_F, k_R and x, to be calculated in this expression, from the first of which the diffusivity will be determined.

3.2. Results and discussion

Besides the amount of absorbed water, i.e. the degree of swelling of the polymer, it is important to study the kinetics of the swelling process. The knowledge of both characteristics — the swelling capacity and the kinetic profile — permits us to decide if a certain polymer is appropriate for a given application. Also, in order to obtain desirable swelling and kinetic properties, some manipulation of copolymerization method and composition can be envisaged. The experimental results of the swelling kinetics for a number of polymers are presented in Tables 1–3. In the last lines of the r columns of these tables, the equilibrium swelling degrees or 'swelling capacities' are, thus, implicitly given.

From Figs. 1–7, the profiles of swelling as a function of the square root of time are shown according to the experimental data of Tables 1–3, as well as the corresponding values calculated from the application of the Berens–Hopfenberg absorption model. (In the figures, the calculated values are joined by a line.) The profiles are plotted as fraction, w, versus $\sqrt{t}$ instead of t, a choice that permits to verify a linear relation for small t — indeed, small absorption [19]. This relation, if present, indicates the predominance of diffusion.

The model equation was applied to the kinetics of the copolymers synthesized and the parameters k_F, k_1 and x, were determined for best fit. This was obtained by minimizing the sum of squares between experimental and calculated values, through a sequential simplex algorithm (based on NAG [17]) implemented by the authors, which permits a closer control over the calculations. Several confirmative calculations were also carried out in Excel. In Table 4, the optimized values for the parameters are shown, together with the water increment, r (equilibrium swelling) for each copolymer, for a better understanding. A dash appears where x was calculated as nearly 0, i.e. a value too small to be considered measurable. With x the weight of the diffusion, $1 - x$ is the weight of the relaxation and, for a particle diameter of $d = 18$ μm, D was finally calculated for each copolymer.

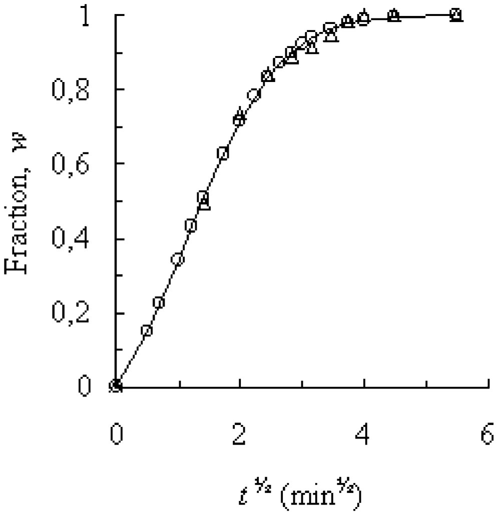

Fig. 2. Kinetics of swelling of polymer C-2: experimental (△) and calculated (○) values.

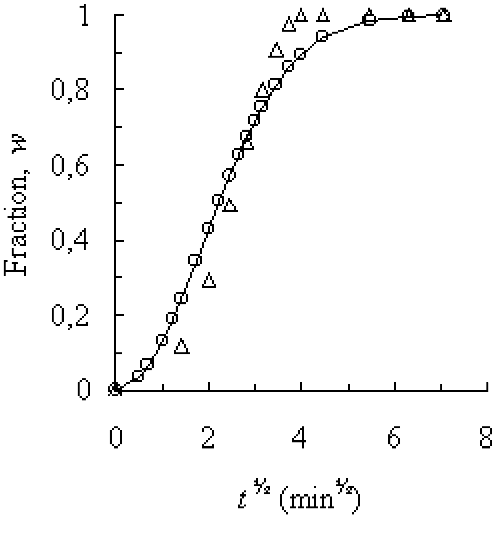

Fig. 1. Kinetics of swelling of polymer C-1: experimental (△) and calculated (○) values.

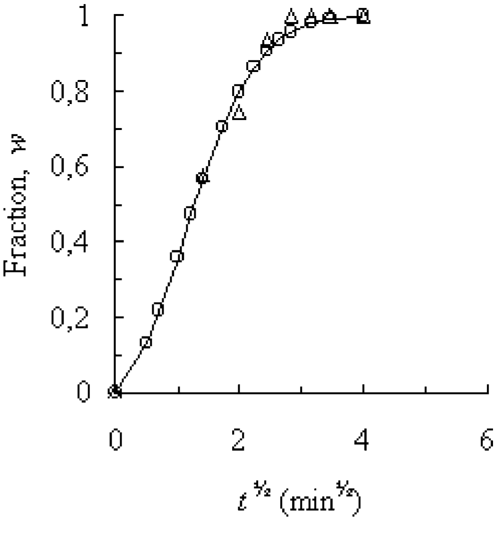

Fig. 3. Kinetics of swelling of polymer C-3: experimental (△) and calculated (○) values.

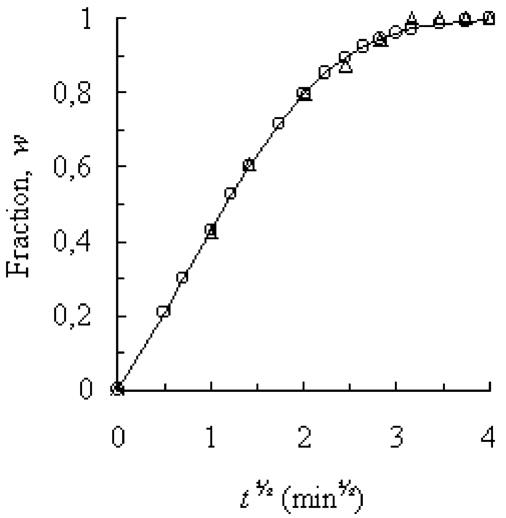

Fig. 4. Kinetics of swelling of polymer C-4: experimental (△) and calculated (○) values.

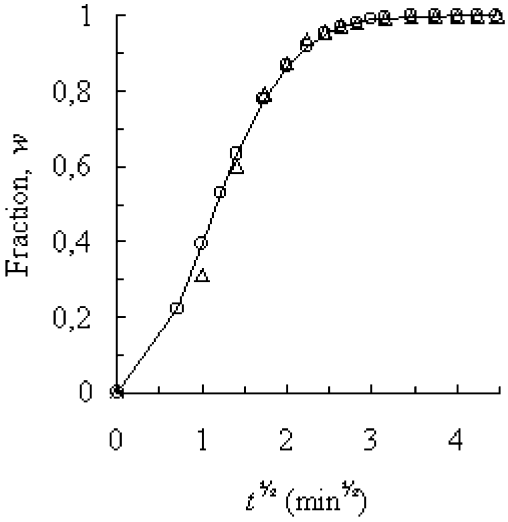

Fig. 6. Kinetics of swelling of polymer C-6: experimental (△) and calculated (○) values.

The swelling of the system water–copolymer results from a mechanism of diffusion and relaxation. The form of the curves, at least in the initial part of the curve (say, up to 50% of the equilibrium swelling), provides an appropriate suggestion of which is the controlling phenomenon. The validity of the model seems to be confirmed by the cases shown, as can be seen in Figs. 1–7, i.e. there is a good agreement between experimental and calculated values. Although most curves may be interpreted as merely showing this good agreement, they are included to reveal some different features, as commented below.

In Figs. 1, 6 and 7, for copolymers C-1, C-6 and C-7, respectively, curves of sigmoid type are found, a form that is typical of the presence of a relaxation contribution. Diffusion is not easy to detect ($x \approx 0$, Table 4), but is plausibly active in the first instants, yielding values of D in the range 2–3 × 10^{-14} cm^2/s.

In Figs. 2–5, the curves show an initial evolution that is closer to a straight line, pointing to a greater influence of diffusion, as confirmed by the values of x in Table 4. Copolymers C-4 and C-5 adhere more to a diffusional process, whereas C-2 and C-3 exhibit an inflection point, characteristic of the relaxation process.

To illustrate the usefulness of the swelling curve to estimate the value of the relaxation constant, the copolymer C-7 was used, once the model indicates a weight of relaxation near unity in this case. A simple calculation, through the annulment of the second derivative of the relaxation expression, $M_{t,\mathrm{R}} = M_\infty[1 - \exp(-k_1 t)]$, yields $t_{\mathrm{infl.}} = 1/(2k_1)$, i.e. $k_1 = 1/2t_{\mathrm{infl.}}$, where $t_{\mathrm{infl.}}$ is the abscissa of the inflection point. In Fig. 8, this case gave $\sqrt{t} \approx 1.04$ or

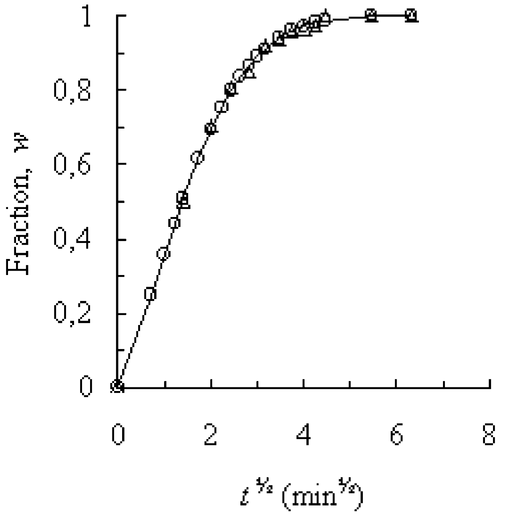

Fig. 5. Kinetics of swelling of polymer C-5: experimental (△) and calculated (○) values.

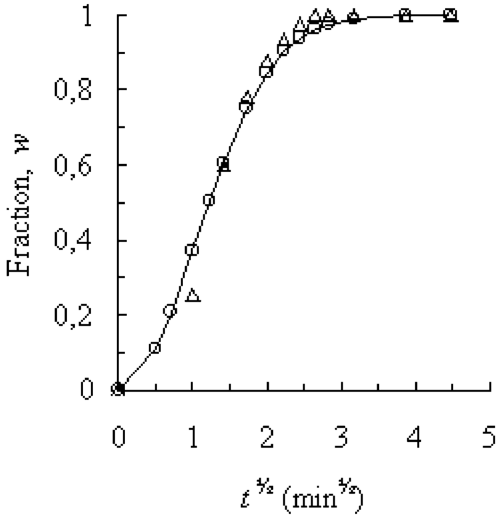

Fig. 7. Kinetics of swelling of polymer C-7: experimental (△) and calculated (○) values.

Table 4
Equilibrium swelling and calculated parameters for the copolymers

	C-1	C-2	C-3	C-4	C-5	C-6	C-7
r_∞	669	420	395	144	466	329	857
x	–	0.32	0.18	0.64	0.41	–	–
$1-x$	1	0.68	0.82	0.36	0.59	1	1
k_F (s^{-1})	1.93×10^{-3}	8.24×10^{-3}	6.75×10^{-3}	5.39×10^{-3}	8.83×10^{-3}	3.71×10^{-3}	3.07×10^{-3}
k_1 (s^{-1})	2.34×10^{-3}	4.04×10^{-3}	6.32×10^{-3}	5.45×10^{-3}	3.15×10^{-3}	8.36×10^{-3}	7.77×10^{-3}
D (m^2/s)	1.58×10^{-14}	6.77×10^{-14}	5.54×10^{-14}	4.40×10^{-14}	7.25×10^{-14}	3.04×10^{-14}	2.52×10^{-14}

$k_1 \approx 7.78\text{E-}3\ s^{-1}$ (7.77×10^{-3} in Table 4). Of course, when the two absorption modes (diffusion and relaxation) are both important, only a rough value is obtained from the estimation of the constant k_1 by the above calculation.

Regarding the values obtained for the parameters, some simple calculations were done in order to verify the sensitivity of the parameters to experimental error in data. As mentioned, the parameters under consideration are k_F — whence, D —, k_1 and x. To that end, a perturbation was imposed on one data point of w, the weight fraction of water absorbed by the polymer.

Among the various copolymers, C-4 was chosen, because it presents comparable contributions of diffusion and relaxation. The perturbation was an increase of 5% in w, from 0.796 for the time $t = 4$ min (Table 2) to 0.836. The resulting perturbed diffusivity value is 3.66×10^{-14} m^2/s, instead of the original 4.42×10^{-14} m^2/s (Table 4), thus an increase of 5% in the data value led to a variation of 17% in the diffusivity, anyway a small effect from the viewpoint of application. To compensate for this effect, the experimental data were determined from triplicate trials, as mentioned, while a broader study would be needed in this domain.

4. Conclusions

A kinetic study of absorption of water by superabsorbents has been performed on synthesized superabsorbent copolymers, since this kinetic behavior is relevant in applications, namely agricultural ones. According to the calculations, the absorption conforms to a model such as the one by Berens–Hopfenberg, which includes Fickian diffusion and a relaxation contribution, in measurable terms.

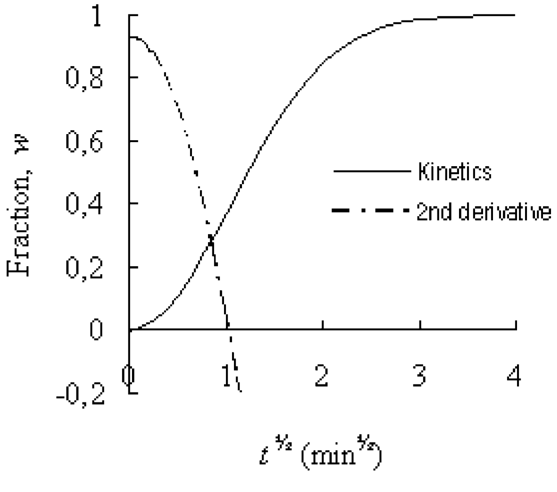

Fig. 8. Kinetic curve of swelling of polymer C-7 (with second derivative in -●-): estimation of k_1.

The seven synthesized copolymers (copolymers C-1–C-7) were based on two monomers, AA and AMPS, with, in the last four cases, a further, crosslink monomer, BA. Two polymerization techniques — free radical solution (for C-1–C-5) and inverse emulsion (for C-6 and C-7) — have been addressed. The following factors intervene in the characteristics of the copolymers studied from the kinetic viewpoint: copolymerization method (solution, inverse emulsion), presence of crosslink agent and pH of the medium.

From the results of the experiments, it is possible to control the degree of swelling and the swelling kinetic behavior by varying the conditions of the synthesis medium. The transport process in the copolymers synthesized with the bifunctional monomer BA by the inverse emulsion technique becomes more non-Fickian, as well as in those copolymers synthesized at rather low pH and without BA.

The copolymers synthesized with BA at higher pH of the reaction medium present a larger swelling degree and the crosslinking density itself can produce this behavior.

Acknowledgements

This research was supported by the 'Centro de Processos Químicos do IST' (Center for Chemical Processes of IST, Technical University of Lisbon, Portugal). We thank the Computing Center of IST.

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