

Smart polymeric membranes: pH-induced non-linear changes in pore size

R. Estrada · R. Rodríguez · V.M. Castaño

Received: 13 November 2009 / Accepted: 19 November 2009 / Published online: 26 May 2010
© Springer-Verlag 2010

Abstract A new kind of synthetic membrane was designed with the capacity to adjust the pore diameter in a wide range of sizes (from 0.8 to 22.3 microns) just by changing the pH of the aqueous medium where it is immersed; in this way it is possible to control externally the pore size of the membrane. A non-linear mathematical model, based on the overlap of the electrical double layers of charged particles, was developed to explain the oscillatory behavior of the pore size when the pH was varied. This model fits correctly this oscillatory behavior. Scanning electron microscope images were obtained in low-vacuum conditions to reduce, as much as possible, possible changes in the external conditions after the immersion in water.

1 Introduction

Polymeric membranes are widely used for filtration and separation processes in a considerable number of applications: reverse osmosis [1–3], water purification [4], chemical and biological separation [5], gas separation, etc. Due these important applications, much effort has been addressed to the design of new membranes with high selectivity and chemical resistance. Nowadays, it is possible to impose on the

membranes an additional requirement related to the possibility of controlling their selectivity externally by changing some external parameters [2].

Cellulose acetate is one of the most commonly used materials for membrane fabrication because it allows the production of membranes with adequate porosity and low binding [6]. Nevertheless, very little effort has been dedicated to produce membranes with externally controlled porosity [4].

In this work the pore size of synthetic polymeric membranes made from cellulose acetate cross linked with polyacrylic acid was determined after they were immersed in aqueous solutions with different pH's. The results show that it is possible to control externally the membrane porosity just by varying the pH of the immersion aqueous solution. The pore size shows a non-linear oscillation as a function of pH. To explain this non-linear behavior, a simple mathematical model based on the overlap of the electrical double layers of two charged particles that approach each other was used to fit the experimental data. For this model three types of forces were included: (a) the repulsion force produced in the overlapping of the electrical double layers of charged polymer molecules, (b) the repulsion force due to the steric interaction produced by the overlapping of the polymer molecules caused by the swelling process and (c) the elastic force produced by changes in the conformational entropy of the molecule. With these terms it was possible to obtain an analytical expression for the dependence of the pore size on the pH; using this expression, the experimental data were well fitted.

2 Experimental

The membranes were synthesized as reported elsewhere [2]. A solution was prepared by dissolving 8 g of cellulose

R. Estrada
Departamento de Física y Matemáticas, Universidad
Iberoamericana, Prol. Paseo de la Reforma 880,
Lomas de Santa Fé, Mexico, DF 01210, Mexico

R. Rodríguez · V.M. Castaño (✉)
Centro de Física Aplicada y Tecnología Avanzada, Universidad
Nacional Autónoma de México, A.P. 1-1010, Querétaro,
Qro. 76000, Mexico
e-mail: castano@fata.unam.mx

acetate (Fluka) in 100 ml of glacial acetic acid (Aldrich) at room temperature. Once the cellulose acetate was completely dissolved, 10 ml of polyacrylic acid with molecular weight of 30 000 g/mol (Aldrich) was added slowly and with medium agitation; this solution was heated at 60°C during 30 min without agitation, allowing the cross-linking reaction between the polyacrylic acid and the cellulose acetate to take place [5, 7–9]. The system was cooled to room temperature and stored at atmospheric pressure during three days. To produce the membranes, the solution was poured on a flat glass mold of 10-cm diameter leaving the mold with the polymer floating on iced water at 4°C for 30 s [10]; then, the mold with the polymer was completely immersed into the same iced water during 15 min until the membrane was completely formed [11, 12]; the membrane thickness was 0.12 mm. The membrane was withdrawn from the iced water and immediately placed into an aqueous solution of controlled pH. The pH was varied from 2 to 12 and in all cases the immersion time was from one to two minutes. The pore size was determined using a low vacuum scanning electron microscope (SEM, JEOL LV 5900) operated at an acceleration voltage of 20 kV and a pressure of 20 Pa. The SEM images of the membranes are reported in Fig. 3a through k. Figure 3a shows the image of the membrane without any immersion in a pH solution (corresponding to pH = 7), which is taken as a reference. Figure 3b through k show the membranes immersed in solutions at different pH's: from 2–6 and 8–12 in steps of 1.

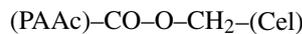
3 Theoretical model

3.1 Membrane morphology

As known, aqueous solutions of polyacrylic acid are polyelectrolytes where the electric charge is due to the deprotonation of the acrylic group: (PAAc)–CO–O⁻; the degree of deprotonation depends on the ionic strength, i.e. the concentration of H⁺. When the ionic strength changes, the polymer molecule suffers deformations caused by a competition between different forces: the Coulombian interactions between charges, the steric interaction force produced by overlap of polymer chains and the elastic forces due to entropic effects. The polymer size can suffer elongations when the electric charge in the molecule is increased (electric repulsion) overcoming the steric and elastic forces; on the other hand, when the charge in the molecules is reduced, the steric and elastic forces can dominate the scenario making the molecule reduce its size to avoid the overlapping with other molecules, recovering its equilibrium size.

The cross-linking reactions are carried out between the hydroxyl group of the PAAc and either the primary hydroxyl

group or the acetate group of cellulose; this produces the following structures:



or



However, not all the OH's or the acetate groups of cellulose react with the hydroxyl groups of the PAAc, essentially due to steric effects; then, some of the un-reacted OH groups of the PAAc are susceptible to deprotonation acquiring a negative charge; the degree of deprotonation depends on the H⁺ concentration, i.e. the pH.

3.2 Electric double layer overlapping

The membrane is a solid network swelled by water. The solid phase (polymer) can suffer expansion or contraction according to the physicochemical properties of the aqueous solution where is immersed. When the polymers swell, they overlap each other increasing locally, in the overlapping region, the monomer concentration producing an osmotic pressure that tries to separate them (steric interaction). When this happens, an elastic force appears produced by changes in the conformational entropy that tends to shrink the size. Additionally, because the PAAc in water is a polyelectrolyte, the electric repulsion between the charges produces an expansion of the molecule; this increment in the particle size also has a contribution to the overlapping between molecules. Then, the double layer overlapping, the steric interaction and the elastic force control the molecule size and consequently the pore size. Then, it is possible to control, to some extent, the pore size of the membrane by changing the ionic strength, i.e. the pH.

An electric system can be fully characterized by determining the electric potential Ψ at every point in space. For charged particles in a continuous medium, using the Debye–Huckel approximation of low potential, the electric potential Ψ can be written as

$$\Psi = \Psi_0 e^{-\kappa x}, \quad (1)$$

where

$$\kappa^2 = \frac{e}{\epsilon k T} \sum_i z_i^2 n_{i0}, \quad (2)$$

where z_i is the valence number of the ions of type i , e the electron charge, n_{i0} the number concentration of ions of type i per unit volume evaluated far from the charged molecule (bulk concentration), ϵ the dielectric constant of the medium, k the Boltzmann constant and T the absolute temperature. κ^{-1} ($\equiv l_D$) is called the 'Debye length of the electrical double layer'.

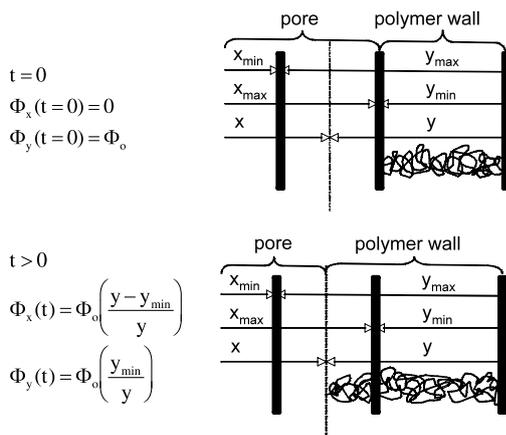


Fig. 1 Schematic diagram, where x measures the changes in the pore size and y the changes in the polymer size

It is possible to obtain the repulsion force F_{DL} per unit area [13, 14] on two charged molecules approaching each other produced by the overlapping of their electric double layers:

$$F_{DL} = 64n_0kT A_0^2 e^{-x/l_D}, \tag{3}$$

where A_0 is a constant that depends on geometry and x is the separation between molecules.

An element of this force taken on an element of area in cylindrical coordinates $dA = 2\pi x dx$ produces

$$f_{DL} = 128\pi n_0kT A_0^2 \int e^{-x/l_D} x dx. \tag{4}$$

When the distance between molecules is small, (4) takes the following shape, after the integration:

$$f_{DL} = cte x^2 - O(x^3). \tag{5}$$

This means that the repulsion force, when the particles approach each other, depends quadratically on the separation distance (terms of higher order are neglected).

The Flory–Krigbaum theory predicts that the free energy depends linearly on the polymer volume fraction that is overlapped. It is possible to show that the polymer volume fraction can be written as (see Fig. 1) [2]

$$\Phi_x(t) = \Phi_0 \left(\frac{y - y_{\min}}{y} \right). \tag{6}$$

With the free energy it is possible to obtain the force due to steric interaction [2]:

$$f_{steric} = 4\pi RT(\chi - 1)N_s\phi_0 \left(x^2 - y_{\min} \frac{x^2}{y} \right), \tag{7}$$

where x and y correspond to the changes in the pore and polymer dimensions (Fig. 1): when the polymer swells the pore size is reduced and vice versa.

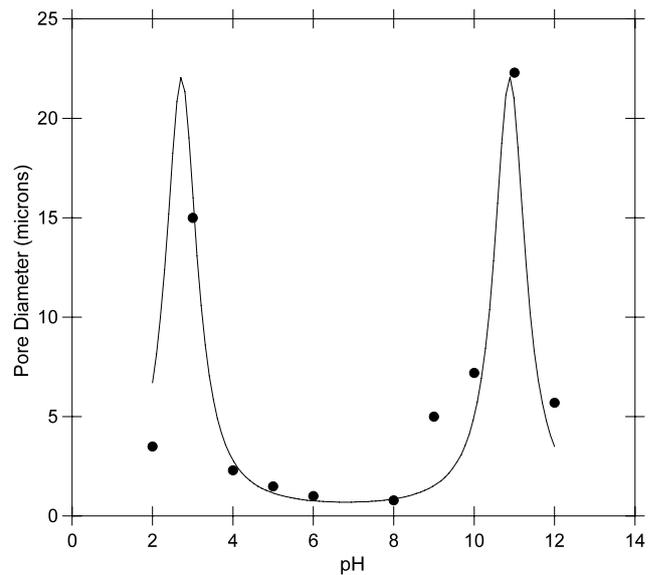


Fig. 2 Plot of pore size versus pH. The continuous line corresponds to the fitting using (14)

The total force contains three contributions: (a) the elastic force due to changes in the conformational entropy of the polymer chains, (b) the force due to steric interactions produced by the concentration gradients (overlap of molecules) and (c) the repulsion force produced by the overlap of the Debye double layer. Then, the total force can be written as

$$f_{total} = k_1x + k_2x^2 - k_3 \frac{x^2}{y}, \tag{8}$$

where k_1 contains contributions of the elastic force which is linear (for small deformations) in the elongation; k_2 contains contributions from the repulsion force produced by the overlapping of the electric double layers, which depends quadratically on the distance (5), while the contribution of the repulsion force produced by the overlap of two molecules (7) is contained in k_2 and k_3 . It can be noticed that the repulsion force due to the double layer interaction has a similar analytical dependence as the steric interaction; this may be due to the similarity that both mechanisms have for the stabilization of colloids or macromolecules in solution: these systems can be stabilized either by electric charge or by steric interaction.

All these processes happen to the polymer molecules of the membrane when it is immersed in a viscous medium; then, the total force should be proportional to the velocity (viscous force), i.e. the rate the molecules move in the fluid; then, (8) can be written as

$$\frac{dx}{dt} = k_1x + k_2x^2 - k_3 \frac{x^2}{y}. \tag{9}$$

A similar situation happens in the y region (Fig. 1), obtaining a similar equation. Then, it is possible to write two

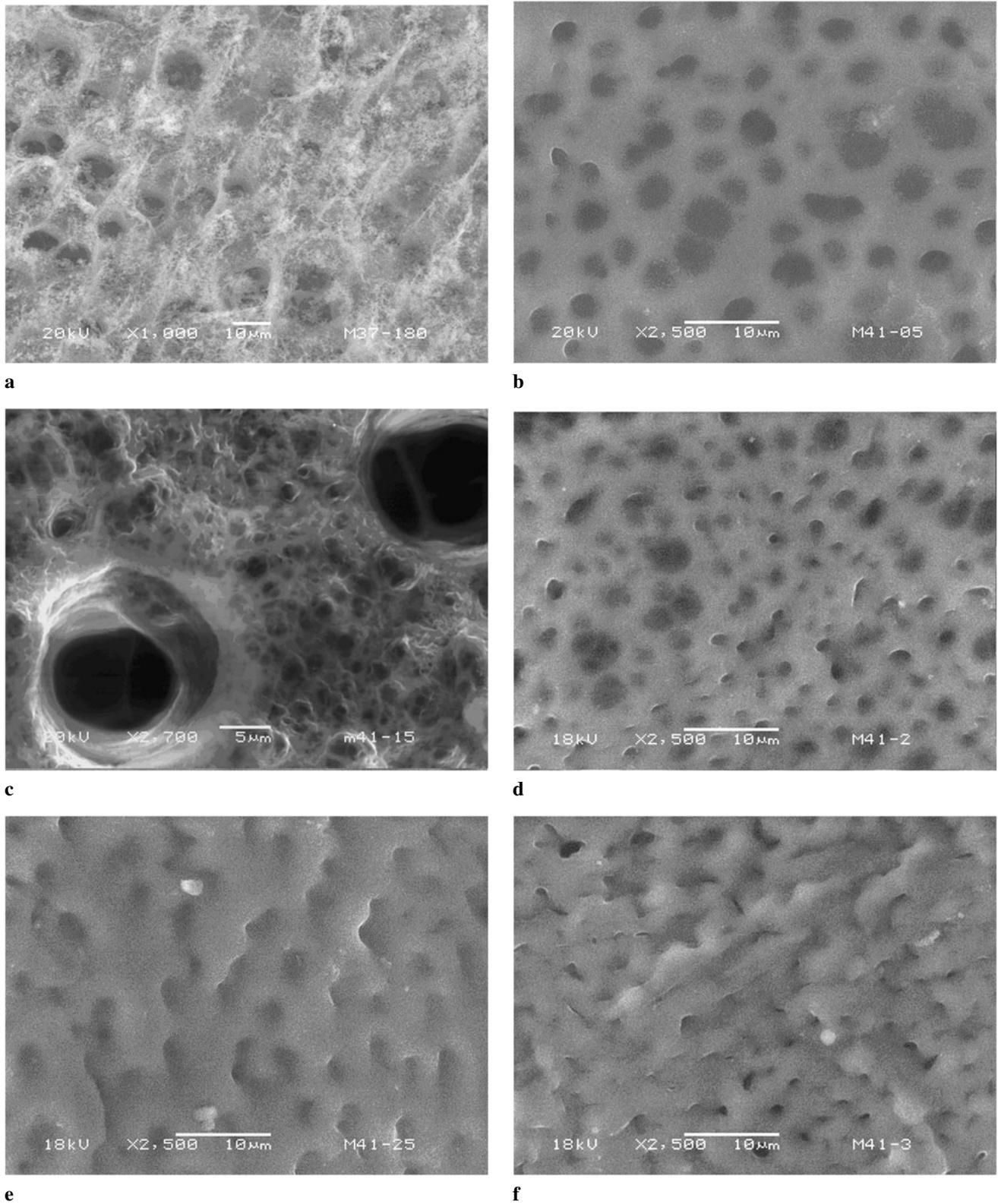
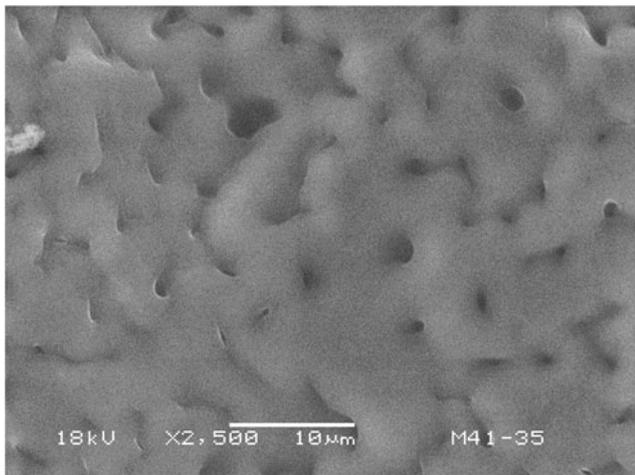
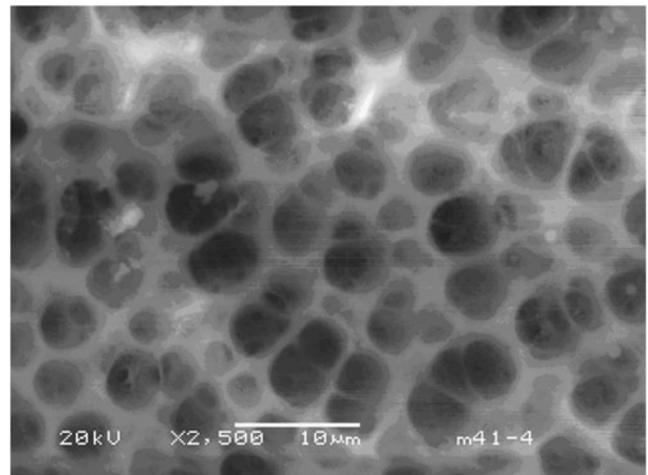


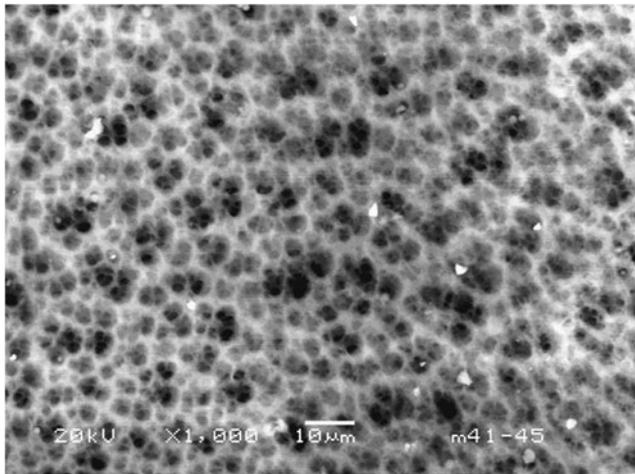
Fig. 3 SEM images of: (a) reference membrane without any immersion in a pH solution, (b–k) membranes immersed in solutions at different pH values: 2, 3, 4, 5, 6, 8, 9, 10, 11 and 12



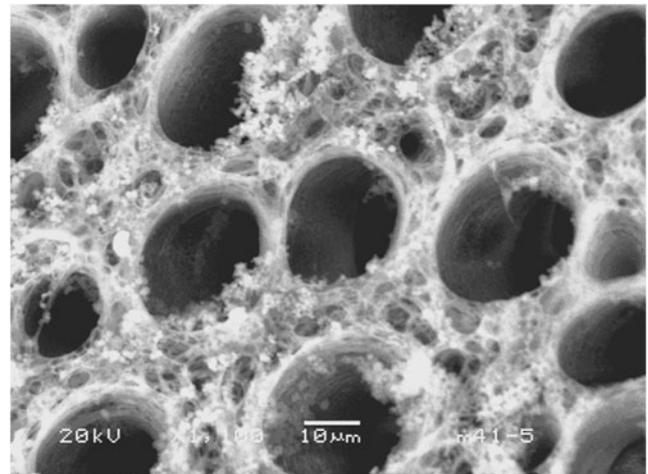
g



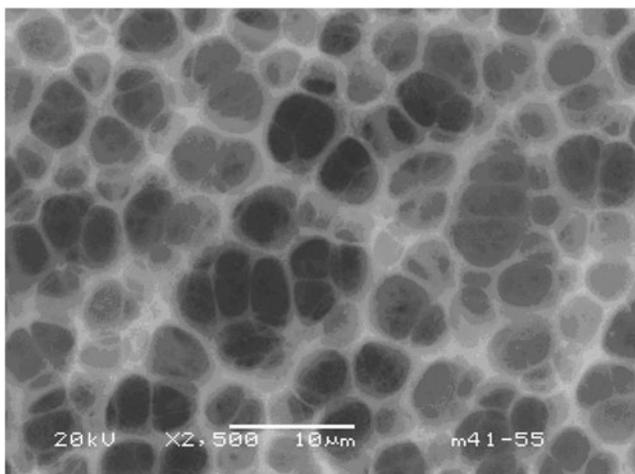
h



i



j



k

Fig. 3 (Continued)

coupled differential equations:

$$\frac{dx}{dt} = k_1x + k_2x^2 - k_3\frac{x^2}{y}; \quad (10)$$

$$\frac{dy}{dt} = k_1y + k_2y^2 - k_3\frac{y^2}{x},$$

which have the solutions

$$x(t) = \frac{x_0}{[1 + a \sin^2(\omega t)]}; \quad (11)$$

$$y(t) = \frac{y_0}{[1 + a \sin^2(\omega t + \delta)]},$$

δ being the phase difference between the x and y variables. The relations between the constants k_i and the parameters a , ω , δ are given by

$$k_1 = \frac{\omega}{\delta} \left(1 - \frac{4}{3}\delta^2\right); \quad k_2 = \frac{\omega}{\delta} (a + 2)\delta^2; \quad (12)$$

$$k_3 = \frac{\omega}{\delta} \left(1 - \frac{2}{3}\delta^2\right).$$

The steady state and the eigenvalues are given by

$$x_{ss} = y_{ss} = \frac{k_3 - k_1}{k_2} = \frac{2}{a + 2} \quad \text{and} \quad (13)$$

$$\lambda = \pm 2i\omega.$$

Since the eigenvalues are imaginary, the solutions oscillate around the steady state. This equation can be written as

$$D = \frac{D_0}{1 + a \sin^2(b(\text{pH}) + \delta)}, \quad (14)$$

where D is the pore diameter and D_0 is the maximum value of the pore size; a and b are fitting parameters and δ is the phase shift related to where the oscillations begin. The experimental data plotted in Fig. 2 were well fitted using (14); the fitting values were: $D_0 = 22.03$; $a = 30.45$; $b = 0.385$; $\delta = -1.05$; as can be noticed, the fitting of the experimental data was good. The continuous line in Fig. 2 corresponds to the fitting using this equation. In Fig. 3a through k are reported images of the pores of the membrane when it is immersed in aqueous solutions at different pH's.

4 Conclusions

It was possible to design synthetic polymeric membranes which possess the property that the pore size can be ad-

justed just by changing the pH of an aqueous solution where they are immersed. The variation in the pore size was in a wide range from 0.8 to 22.3 microns when the pH was varied from 2 to 12. The pore size depends in a non-linear cyclic way on the pH. A mathematical model was developed to explain this non-linear behavior. The model was based on three different mechanisms: the forces produced by the overlapping of the electric double layers when two charged particles approach each other, the forces produced by the overlapping of the polymer molecules when they are swelled by the medium (Flory–Krigbaum theory) and the elastic force due to conformational entropy changes. The experimental data were well fitted using this model. The design of these membranes open the possibility of using them in situations where there is required the adjustment of the pore size with pH to fulfill some specific function.

References

1. Y. Osada, T. Nakagawa, *Membrane Science and Technology* (Dekker, New York, 1992), pp. 239–358
2. R. Rodríguez, V.M. Castaño, *Appl. Phys. Lett.* **87**, 144103 (2005)
3. F.A. Ruiz-Treviño, D.R. Paul, *J. Appl. Polym. Sci. Part B* **36**, 1037 (1998)
4. U. Merten, *Desalination by Reverse Osmosis* (MIT Press, Cambridge, 1966), pp. 55–89
5. R.A. Bartsch, J.D. Way, *Chemical Separation with Membranes*. ACS Symp. Ser. (American Chemical Society, Washington, 1996), pp. 57–74
6. S. Park, J. Crank, *Diffusion in Polymers* (Academic Press, San Diego, 1968), pp. 277–319
7. R.W. Baker, *Membrane Technology and Applications*, 2nd edn. (Wiley, New York, 2004)
8. I. Pinnau, *Advanced Materials for Membrane Applications* (American Chemical Society, Washington, 2004), pp. 1–23, 106–128 and 269–280
9. G. Odian, *Principles of Polymerization* (Wiley, New York, 1981)
10. P. Hillis (ed.), *Membrane Technology in Water and Waste Water Treatment* (Royal Chem. Soc., London, 2000), pp. 25–31, 57–66 and 150–157
11. W.R. Vieth, *Membrane Systems Analysis and Design* (Wiley, New York, 1994), pp. 1–128
12. N. Toshima, *Polymers for Gas Separation* (VCH, Weinheim, 1992)
13. P.C. Hiemenz, *Principles of Colloids and Surface Chemistry* (Dekker, New York, 1986)
14. E.J.W. Verway, J.T.H. Overbeek, *Theory of the Stability of Lyophobic Colloids* (Elsevier, Amsterdam, 1948)