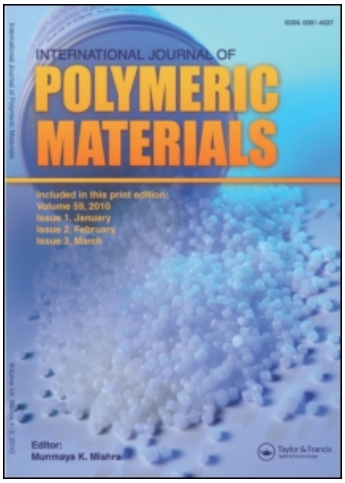


International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

Smart polymeric membranes with adjustable pore size

R. F. Estrada[ab]; R. Rodríguez[c]; V. M. Castaño[c]
[a] Departamento de Física, Universidad Iberoamericana, Lomas de Santa Fé, México [b] Posgrado en Ingenieria, Universidad Autónoma de Querétaro, Querétaro, México [c] Instituto de Física, UNAM, Querétaro, México

Online publication date: 27 October 2010

To cite this Article Estrada, R. F. , Rodríguez, R. and Castaño, V. M.(2003) 'Smart polymeric membranes with adjustable pore size', International Journal of Polymeric Materials, 52: 9, 833 — 843
To link to this Article: DOI: 10.1080/713743715
URL: http://dx.doi.org/10.1080/713743715

International Journal of Polymeric Materials, 52:833–843, 2003

ISSN: 0091-4037 print/1543-5253 online
DOI: 10.1080/00914030390231870

Taylor & Francis
Taylor & Francis Group

SMART POLYMERIC MEMBRANES WITH ADJUSTABLE PORE SIZE

R. F. Estrada
Departamento de Física, Universidad Iberoamericana, Lomas de Santa Fé, México and Posgrado en Ingenieria, Universidad Autónoma de Querétaro, Querétaro, México

R. Rodríguez and V. M. Castaño
Instituto de Física, UNAM, Querétaro, México

A synthetic membrane prepared by crosslinking two different organic polymers is reported. The porosity of this membrane can be adjusted at will, simply by changing the time the membranes are immersed in a warm liquid at 60°C. The pore size of this membrane can be adjusted from 1 micron to nearly 50 microns, allowing to cover a wide range of potential applications. The pore size shows a periodic behavior with the immersion time.

Keywords: adjustable pore size, polymeric membrane, annealing temperature

1. INTRODUCTION

The use of polymeric membranes for filtration and separation processes is an important research field that has attracted the attention of scientists due to their wide range of scientific and technological applications. Among the important applications one can mention: reverse osmosis [1–3], water purification, gas separations [2, 4], biological separation processes [5], etc.

An important area of development in this research field is the design of new polymeric materials or new morphological structures with the appropriate properties capable of fulfilling the requirements imposed on the membranes during actual use. High chemical and mechanical stability is always required, together with a tough control of the pore size and its corresponding distribution. Having open pores

Received 12 April 2001; in final form 11 May 2001.
Address correspondence to V. M. Castaño, Instituto de Física, UNAM, A.P. 1-1010, Querétaro, Qro. 76000, México. E-mail: meneses@servidor.unam.mx

through all the material that form the membrane, is also an important feature, increasing the efficiency of the membrane.

One important achievement in this field is the possibility to control pore size of the membrane and its distribution. In some cases, specific compounds, ground to the required specific size, are mixed with the polymer to form the membrane; after this, the membrane is subjected to a thermal treatment in order to remove the compound and thus form the pore. This compound is generally removed by dissolution or sublimation. This procedure allows to produce membranes with specific pore sizes, but once this pore size is specified, the membrane's morphology is fixed.

In this work, a novel kind of membranes is reported where the pore size can be adjusted at will, in the very same membrane. That is, the pore size can be adjusted in a wide range of sizes, allowing to change the porosity of the membrane without having to change the membrane itself. The change in pore size is accomplished simply be changing the time the membrane is immersed in a warm liquid at 60°C. These membranes were obtained by crosslinking cellulose diacetate and poly(acrylic acid) [6].

2. EXPERIMENTAL

The membranes were produced by dissolving 8 g of cellulose acetate (Fluka Chem.) in 100 ml glacial acetic acid (Aldrich Co.) at room temperature. Once a transparent solution was obtained, 10 ml of 35% aqueous solution of poly(acrylic acid) (Aldrich Co.) with a molecular weight of 15000 g/mol was added to the solution and heated at 60°C for 30 min. The solution was allowed to cool down to room temperature and stored for three days.

Several membranes were cast by pouring the solution in a flat glass mold of 10 cm diameter floating on an ice-mixture at 4°C for 30 sec. Then, the whole mold with the solution was immersed in the same cold water for few minutes. The thickness of the resulting membranes was 0.07 cm.

Once the membranes were formed, they were removed from the glass substrate and washed in this water for few minutes. Finally, each membrane was immersed into warm water at 60°C for different periods of time: from 0.5 to 5.0 minutes in a half a minute steps. Eleven samples were prepared with different immersion times in the warm water.

The pore size of these membranes was determined by using a low vacuum Scanning Electron Microscope JEOL LV 5900 operated with an accelerating voltage of 20 kV and a pressure of 18 Pa.

3. RESULTS AND DISCUSSION

The SEM micrographs of the membranes at different immersion times are shown in Figures 1a through 1k. Figure 1a shows the porosity of the membrane without immersion into the warm water, whereas the others correspond to a different immersion times, from 0.5 min. to 5.0 min. in steps of 0.5 min. (Figures 1b to 1k). From these micrographs the pore size was determined by measuring all the pores in the micrograph and taking the average, which is reported in Figure 2, where a plot of the average pore size versus the immersion time is shown. As observed there, the pore size changes with the immersion time. Also notice that the pore size has a periodic dependence with the immersion time.

This periodic dependence of the pore size on the immersion time can be explained by analyzing the two effects that are present in the system. On the one hand, we have the segregation effects between the two polymers that form the membrane, and on the other the partial miscibility produced by the thermal treatment applied to the membrane by immersing it in the warm water. These two effects complete

(a)

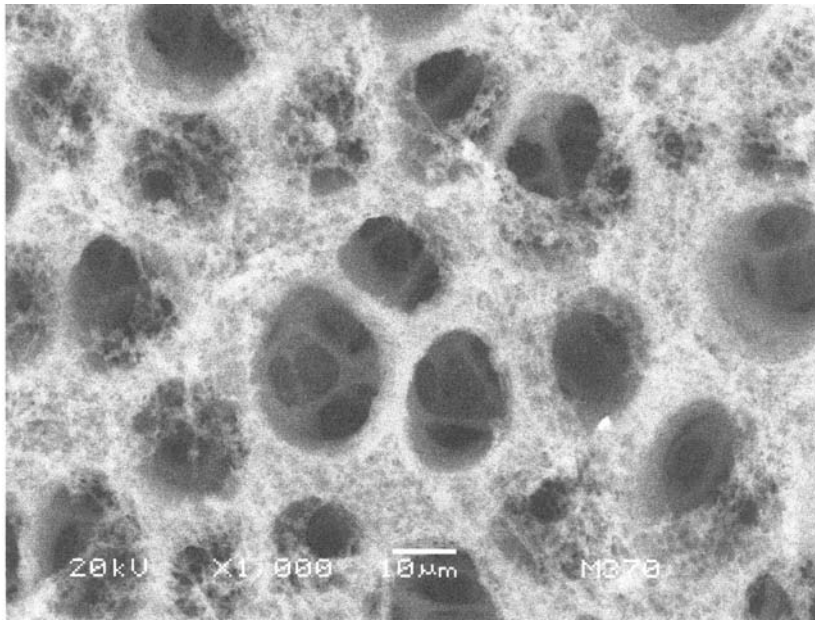


FIGURE 1 Series of SEM micrographs. From 1a through 1k corresponds to membranes immersed for different periods into warm water (60°C, 0 min. through 5.0 min., respectively). (*Continued*).

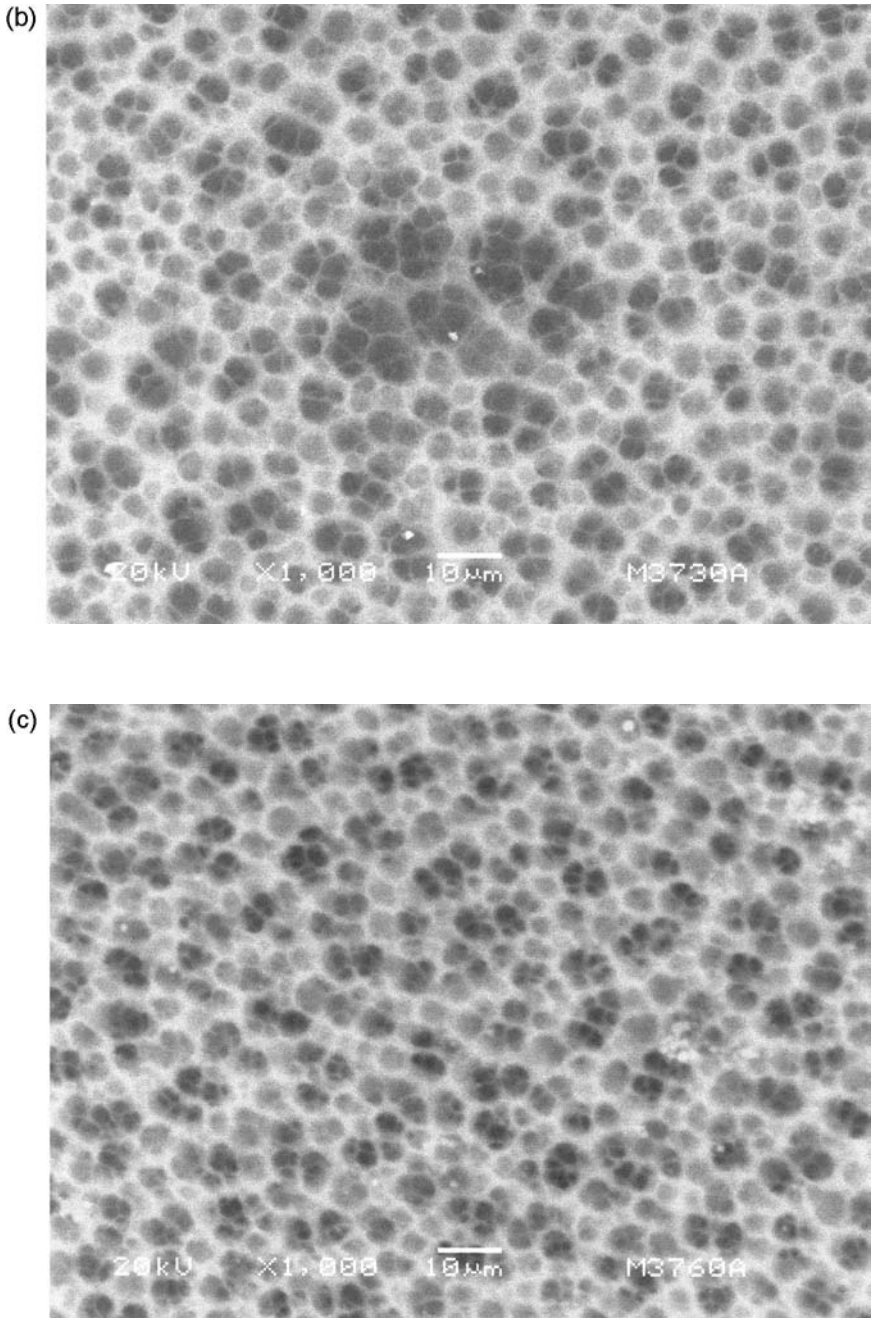
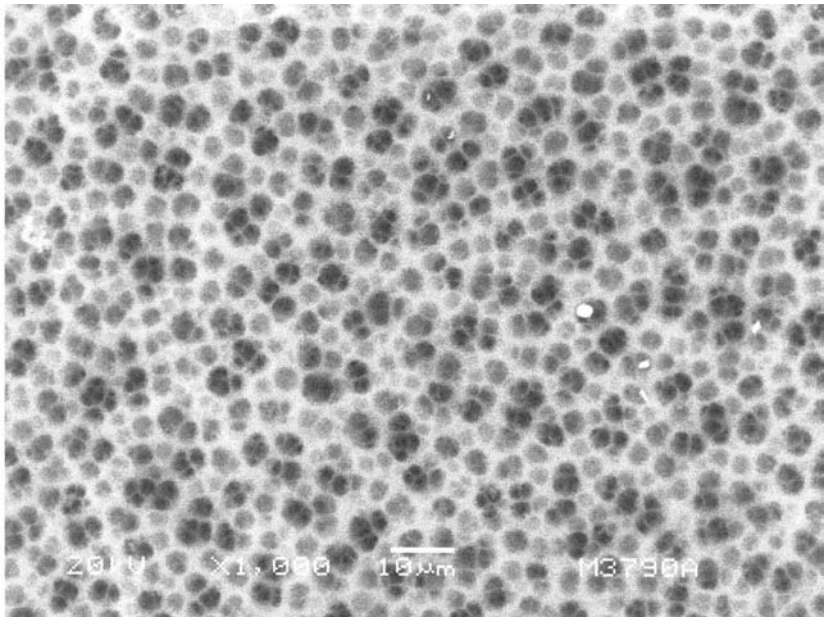


FIGURE 1 (*Continued*).

(d)



(e)

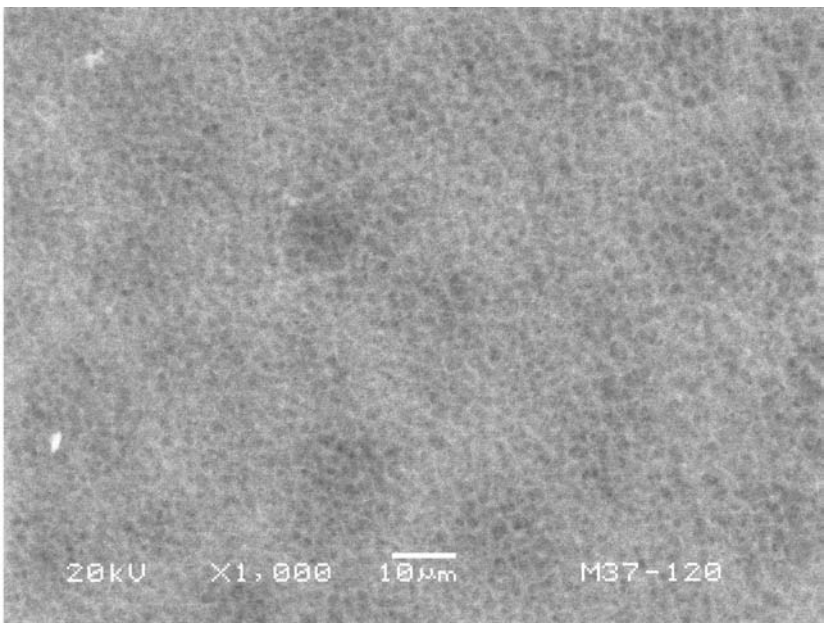


FIGURE 1 (*Continued*).

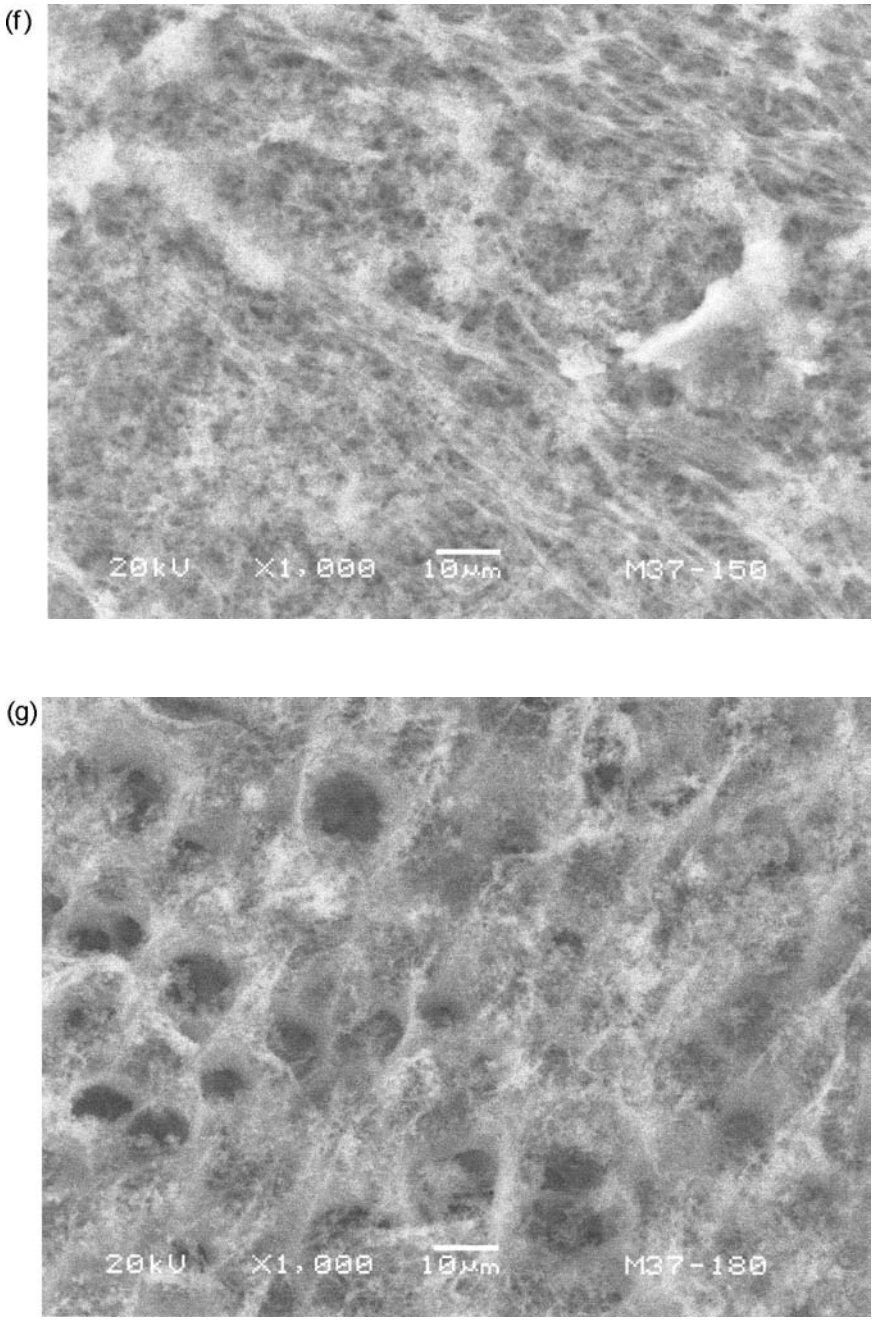
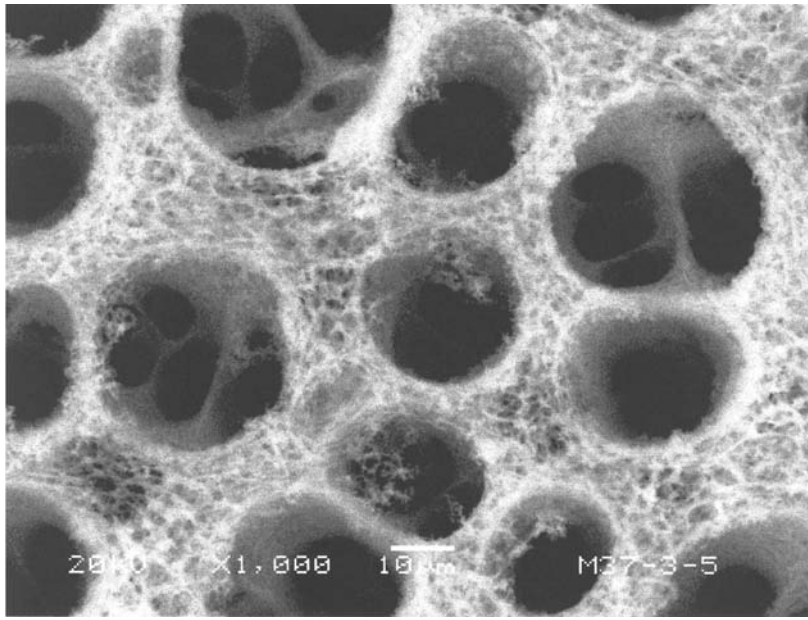


FIGURE 1 (*Continued*).

(h)



(i)

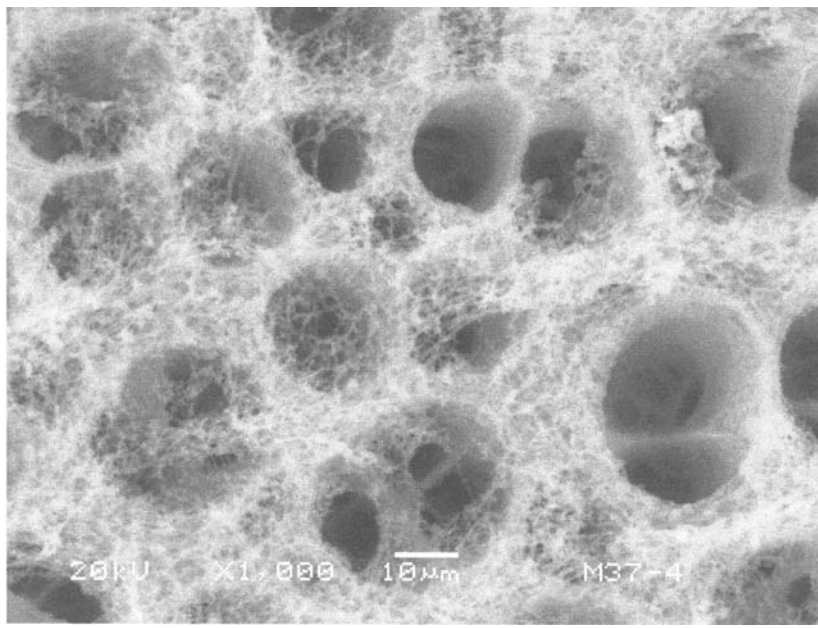
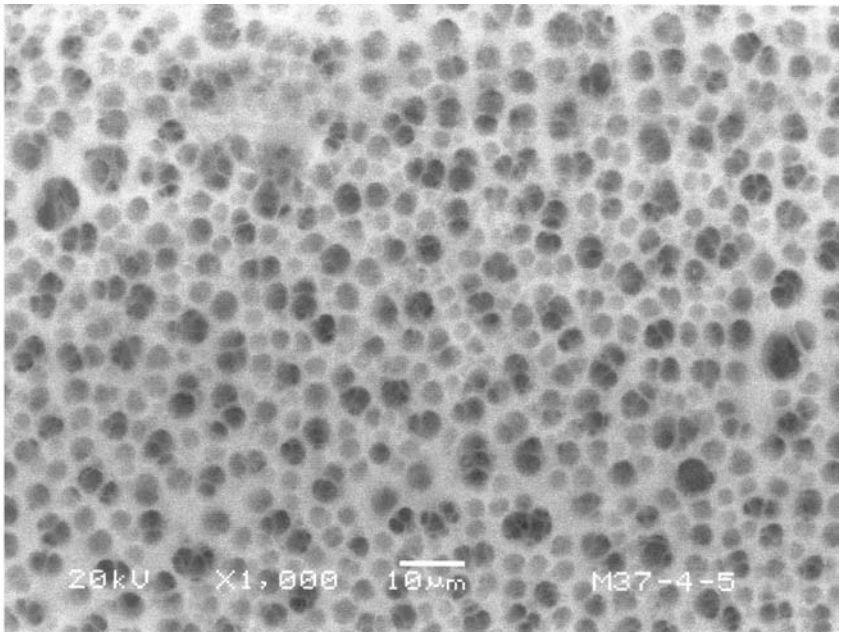


FIGURE 1 (*Continued*).

(j)



(k)

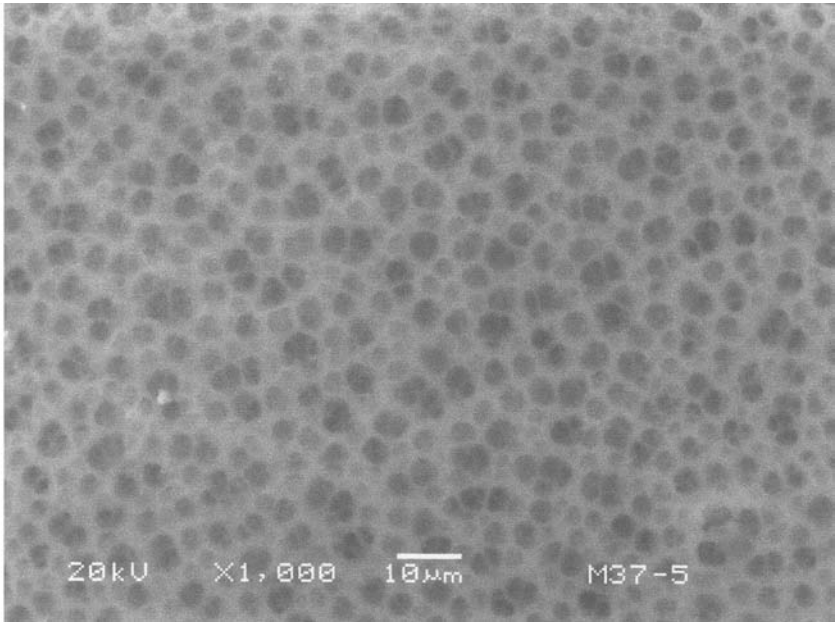


FIGURE 1 (*Continued*).

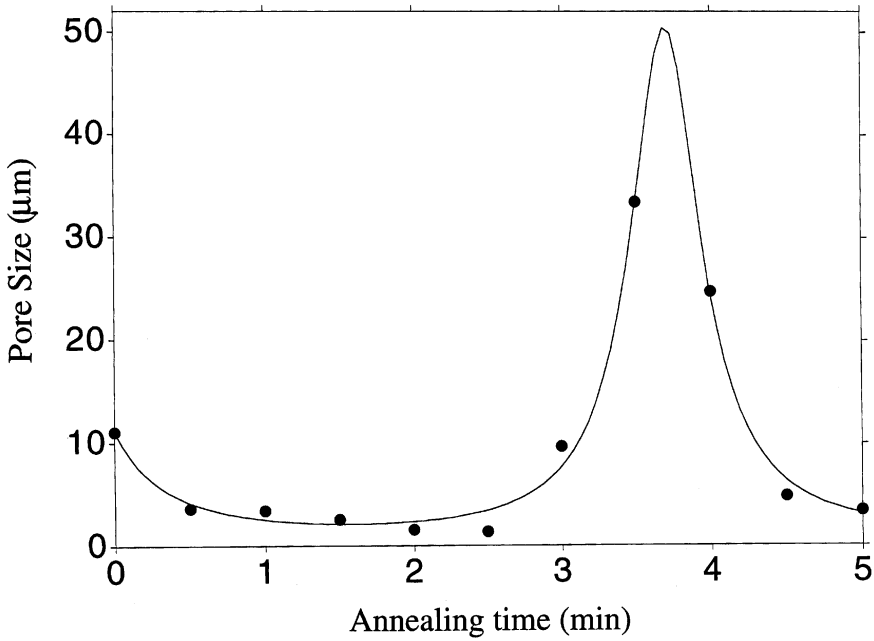


FIGURE 2 Plot of the average pore size as a function of the immersion time. The points correspond to the experimental values while the continuous line to the fitting using equation (1) and the values reported in the text.

with each other to change the morphology of the membrane, thus modifying the pore size.

The experimental points reported in the plot in Figure 2 can be well fitted by using the equation:

$$P = \frac{P_o}{[1 + a \sin^2 b(t - t_o)]} \tag{1}$$

where P is the pore size at some particular immersion time t; P_o, t_o are the maximum pore size and the immersion time corresponding to this maximum pore size; a and b are fitting parameters related with the miscibility properties of the cellulose and poly acrylic acid, and with properties like the thickness of the membrane, the molecular weight of both polymers and the chemical composition of the whole membrane. The physico-chemical details of this equation, along with a mathematical model to explain this behavior, will be reported separately.

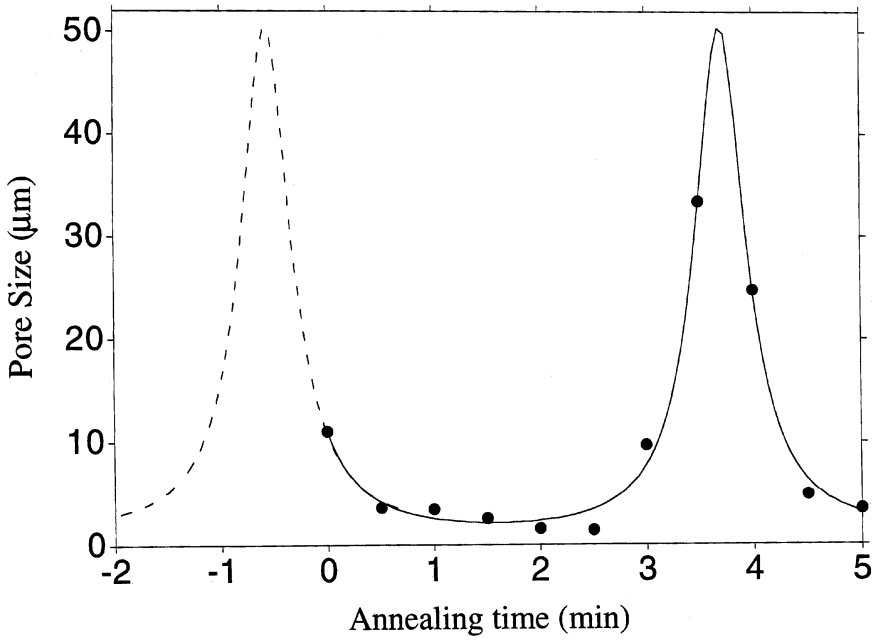


FIGURE 3 Plot of the average pore size as a function of the immersion time but with an extrapolation to early times. The time for attaining a maximum pore size and the overlap between the extrapolation and the real data can be appreciated.

In the present case, the best fit was obtained for:

P_o = 50.54 microns
t_o = −0.556 min.
a = 22.57
b = 0.738

The continuous line in Figure 2 corresponds to the fitting obtained using equation (1) with the aforementioned values.

From the fitting one can observe that the maximum pore size obtained for the membranes prepared as above is nearly 50 microns and these maxima occur at the times $t_o = -0.556$ min. and $t_o = +3.68$ min. From these values it is possible to evaluate the period and the frequency of the oscillation, resulting: $T = 4.24$ min. and $f = 0.236$ rpm.

Figure 3 contains an extrapolation to lower times, where a good overlapping between the experimental data and the extrapolated

curve and the time $t_o = -0.556$ min. is clearly shown to correspond to a maximum value of the pore size.

4. CONCLUSION

A polymeric membrane produced by mixing two different organic polymers is reported. This membrane has the ability to change the pore size just by changing the immersion time in warm water, allowing to change at will this important parameter, thus making it possible to control the flow and selectivity of specific species passing through the membrane. This adjustable membrane is part of a series of intelligent membranes that we are currently designing, where the pore size can be controlled by changing some specific external parameter such as pH, temperature, incident light, etc.

REFERENCES

[1] Osada, Y. and Nakagawa, T. (1992). *Membrane Science and Technology*, Marcel Decker, New York.
[2] Buyanov, A. L., Revelskaya, L. G., Kuznetzov, Y. P. and Shestakova, A. S. (1998). *J. Appl. Polym. Sci.*, **69**, 761.
[3] Merten, U. (1966). *Desalination by Reverse Osmosis*, MIT Press, Boston.
[4] Ruiz-Treviño, F. A. and Paul, D. R. (1998). *J. Appl. Polym. Sci.*, **B36**.
[5] Park, S. and Crank, J. (1968). *Diffusion in Polymers*, Academic Press, New York.
[6] Estrada, R. F. and Castaño, V. M. *Polym. Bull* (in Press).