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Separation Science and Technology

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713708471>

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To cite this Article Bottino, A. , Capannelli, G. , Petit-bon, P. , Cao, N. , Pegoraro, M. and Zoia, G.(1991) 'Pore Size and Pore-Size Distribution in Microfiltration Membranes', *Separation Science and Technology*, 26: 10, 1315 — 1327

To link to this Article: DOI: 10.1080/01496399108050534

URL: <http://dx.doi.org/10.1080/01496399108050534>

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Pore Size and Pore-Size Distribution in Microfiltration Membranes

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Abstract

This paper deals with the characterization of microfiltration membranes by porosimetric measurements. Different methods have been used to test the membranes: the Poiseuille–Knudsen method, the mercury intrusion method, and liquid displacement porometry. Membranes were also examined with the aid of a scanning electron microscope. On the basis of the results obtained, liquid displacement porometry was proven the only method applicable for a proper characterization of the membranes.

INTRODUCTION

The measurement of pore size and pore size distribution is very important in the evaluation and characterization of porous membranes; in particular, ultra and microfiltration membranes. Ultrafiltration (UF) membranes generally present pore radii from 1.5 to about 50 nm. In microfiltration (MF) membranes, they can reach many hundreds of nanometers.

Different experimental methods can be employed to evaluate membrane porosity (1–3). Some of them, such as bubble pressure (4, 5) and the Poiseuille–Knudsen method (6, 7), give the maximum and mean pore radius, respectively. Other methods supply a pore radius distribution. Among these methods are mercury porosimetry (8), permoporometry (9, 10), thermoporometry (11, 12), and gas (13) or liquid displacement porometry (LDP) (14–20).

The latter method has been extensively used (17–20) to evaluate porosity of UF membranes. The procedure first applied by Erbe (14) has

been modified and refined, and an automatic computer instrument has been developed (19, 20).

In the present work we extend the use of LDP to the characterization of MF membranes and compare the porosimetric data with those obtained by other techniques such as the Poiseuille–Knudsen method (PK) and the mercury intrusion method (MI).

EXPERIMENTAL

Materials

Porous microfiltration membranes of polysulfone (Gelman Science Inc. HT 200) and nylon 66 (Pall Europe Ltd) were employed. The nominal pore radius declared by the manufacturers was 200 nm for both membranes.

Poiseuille–Knudsen Method (PKM)

The method allows determination of only the mean pore radius. Of the methods used in this work, PKM is the least known one and therefore it will be briefly described.

Having named Φ the gas molar flux passing through a membrane, Yasuda and Tsai (6) defined a particular specific flux \bar{J} :

$$\bar{J} = \Phi RT \quad (1)$$

where T is the temperature and R is the gas constant. In the steady-state regime, \bar{J} is independent of the pressure inside the membrane.

The general expression for the gas flux \bar{J} through a porous membrane in the viscous Knudsen regime is

$$\bar{J} = K \frac{\Delta P}{l} \quad (2)$$

where K is the permeability coefficient and ΔP is the pressure difference through a membrane of thickness l .

The permeability coefficient, K , can be expressed as (21, 22)

$$K = \left(K_0 + \frac{B_0 \bar{P}}{\eta} \right) \quad (3)$$

where K_0 and B_0 are defined as the Knudsen permeability coefficient and the geometric factor of the membrane, respectively; η is the gas viscosity; and \bar{P} is the mean pressure of the gas passing through the membrane pores.

Following Carman (21):

$$K_0 = \frac{4}{3} \frac{\delta}{k_1} \frac{\epsilon m \bar{v}}{t^2} \quad (4a)$$

and

$$B_0 = \frac{\epsilon m^2}{K_0 t^2} \quad (4b)$$

where K_0 and δ/k_1 are assumed constants and, as suggested by Carman (21), are considered to have the values of 2.5 and 0.8, respectively; ϵ is the membrane porosity; t is the tortuosity factor; m is the hydraulic pore radius, i.e., the ratio of the hole section area to its wet perimeter; and \bar{v} is the mean velocity of the gas of molecular mass M :

$$\bar{v} = \left[\frac{8RT}{\pi M} \right]^{1/2} \quad (5)$$

Combining Eqs. (2), (3), (4), and (5) gives

$$m = \frac{B_0}{K_0} \cdot \frac{16}{3} \cdot \left[\frac{2RT}{\pi M} \right]^{1/2} \quad (6)$$

Equation (6) allows the hydraulic radius to be calculated without porosity and tortuosity factor measurements. In our experiments, K_0 is obtained by extrapolation of K versus \bar{P} at $\bar{P} = 0$. B_0 is obtained by multiplying the slope of the same function by the gas viscosity η .

K is evaluated starting from the experimental flow rate, J^* (expressed in mL/h), measured by a rotameter. In fact, J^* is related to the gas molar flux Φ through the equation

$$\Phi = \frac{J^*}{3600 \cdot 22.4 \cdot A} \quad (7)$$

where A is the membrane area.

From knowledge of Φ , one can obtain \bar{J} (from Eq. 1) and finally of K (from Eq. 2).

Figure 1(a) shows the apparatus used in the pressure range from 0.1 to 0.18 MPa; Fig. 1(b) shows the same apparatus for pressures lower than 0.1 MPa.

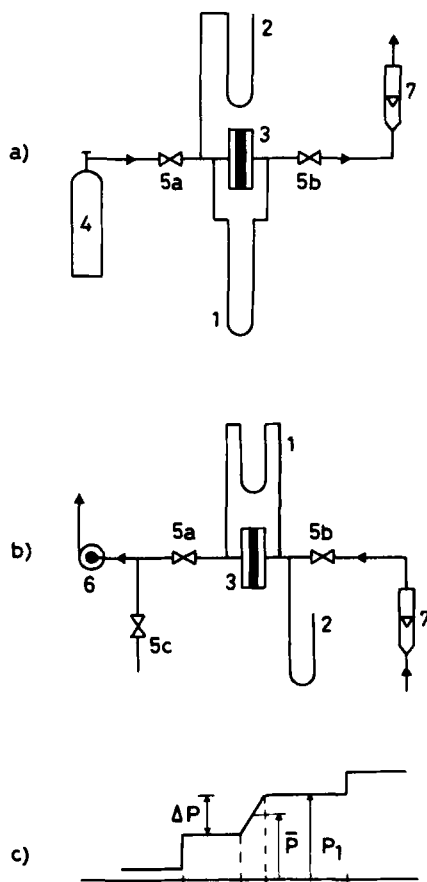


FIG. 1. Schematic diagram of the experimental set-up used for gas permeability measurements. Differential manometer (1); mercury manometer (2); membrane holder (3); compressed air bottle (4); valves (5); vacuum pump (6); flowmeter (7).

In the scheme shown in Fig. 1(a), air is driven from a bottle (4) to the upstream membrane face. Upstream pressure is adjusted by a valve (5a) and measured by a manometer (2). Downstream pressure is controlled by a valve (5b). ΔP is measured by a differential manometer (1). The mean pressure \bar{P} is $P_1 - \Delta P/2$ (Fig. 1c). Gas flow is measured by a flowmeter (7) operating at atmospheric pressure.

In Fig. 1(b), air enters the apparatus at atmospheric pressure and is driven by a vacuum pump (6). Flux is measured by the flowmeter (7) and reaches the membrane at a pressure adjusted by a valve (5b). Valve (5a) controls the downstream pressure. The value of the upstream pressure is

obtained by manometer (2), and the differential pressure value ΔP by manometer (1).

Mercury Intrusion Method (MI)

The experiments were carried out using a mercury porosimeter (Carlo Erba Strumentation series-2000). Pore radius was calculated by using Cantor's equation:

$$r = \frac{2\gamma \cos \Theta}{P} \quad (8)$$

where P is the pressure at which pores of radius r are intruded; γ is the surface tension and Θ is the contact angle.

By using $\Theta = 141.3^\circ$ and $\gamma = 0.484 \text{ Pa}\cdot\text{m}$, Eq. (8) becomes

$$r \text{ (nm)} = \frac{750}{P \text{ (MPa)}} \quad (9)$$

Because the instrument had a maximum operating pressure of 200 MPa, pores up to 3.75 nm were examined.

Liquid Displacement Porometry (LDP)

The measurements were carried out at 20°C with the automatic device described in Refs. 19 and 20 by using a pair of immiscible liquids obtained from the demixing at 20°C of a mixture of 1-pentanol and bidistilled water in a volumetric ratio of 50/50. The interfacial tension between the two phases was $\gamma = 48 \times 10^{-4} \text{ Pa}\cdot\text{m}$ at 20°C . The alcohol phase was forced through the membrane previously filled with water.

The flux of the alcohol phase was increased stepwise by means of the programmable volumetric pump of the instrument, and the equilibrium pressure for each step of the flux was monitored and recorded. The pore permeability (flux/pressure) vs pore radius curve was obtained from flux and pressure data through Cantor's equation with $\cos \Theta = 1$ and $\gamma =$ interfacial tension. Pore number and pore area vs pore radius curves were obtained by combining Cantor's equation with the well-known Hagen-Poiseuille relationship.

RESULTS AND DISCUSSION

In order to obtain preliminary information on pore sizes and their distribution, membrane surfaces were examined with a scanning electron

microscope (Cambridge Stereoscan). The procedure used to prepare specimens for microscopy observation is described in Ref. 23.

Scanning electron micrographs taken at different magnifications of the upper surfaces of nylon 66 (Ny) and polysulfone (PSF) membranes are shown in Figs. 2 and 3, respectively. As can be seen, both membranes exhibit pores of various sizes and only a few of them have radii close to 200 nm. The lower surfaces were also examined, and they appeared similar to the upper ones.

Table 1 lists pore radii evaluated by different porosimetric methods. The tabulated figures do not agree among themselves, and as far as the mean pore radii, \bar{r} , are concerned, they are often different from the ones listed by the manufacturers.

The largest variation (about 100%) in \bar{r} obtained by the PK method should not be related to a lack of accuracy of gas permeation measurements, since a straightforward relationship between the permeability coefficient K and the mean pressure \bar{P} holds (Figs. 4 and 5). Altena et al. (7) used the gas permeation method to characterize UF and reverse osmosis membranes, and they obtained noticeable different \bar{r} values depending on the type of gas used to perform the measurements. Our results seem to confirm the inadequacy of the PK method to determine mean pore radius, even for microfiltration membranes.

Figures 6 and 7 show the porosimetric results obtained by the MI method. As can be seen, both membranes present very narrow pore size distribution curves with a maxima in the 300–600 nm range. Even in this case the values of \bar{r} (Table 1) are far from the ones declared by the manufacturers. This fact can be attributed to the high pressures used in the MI method which causes membrane compaction as well as the formation of microfractures with consequent alteration of pore shape and size. On the basis of these results it is concluded that the MI method is not applicable for the characterization of porous membranes.

Figures 8 and 9 show cumulative distribution curves obtained by LDP. The basic advantage of this method is that the membrane is tested in wet conditions, i.e., very close to the ones used during membrane service, and that the pressure necessary to detect pores of even a few nanometers is too low to cause membrane compaction. As shown in Figs. 8 and 9, both membranes exhibit broad pore size distributions. These results are qualitatively consistent with the microscopy observations of membrane surfaces reported in Figs. 2 and 3. Table 1 shows that the value of \bar{r} obtained by LDP is very close to 200 nm. The results obtained indicate the usefulness of LDP in determining pore size and their distribution in MF membranes.

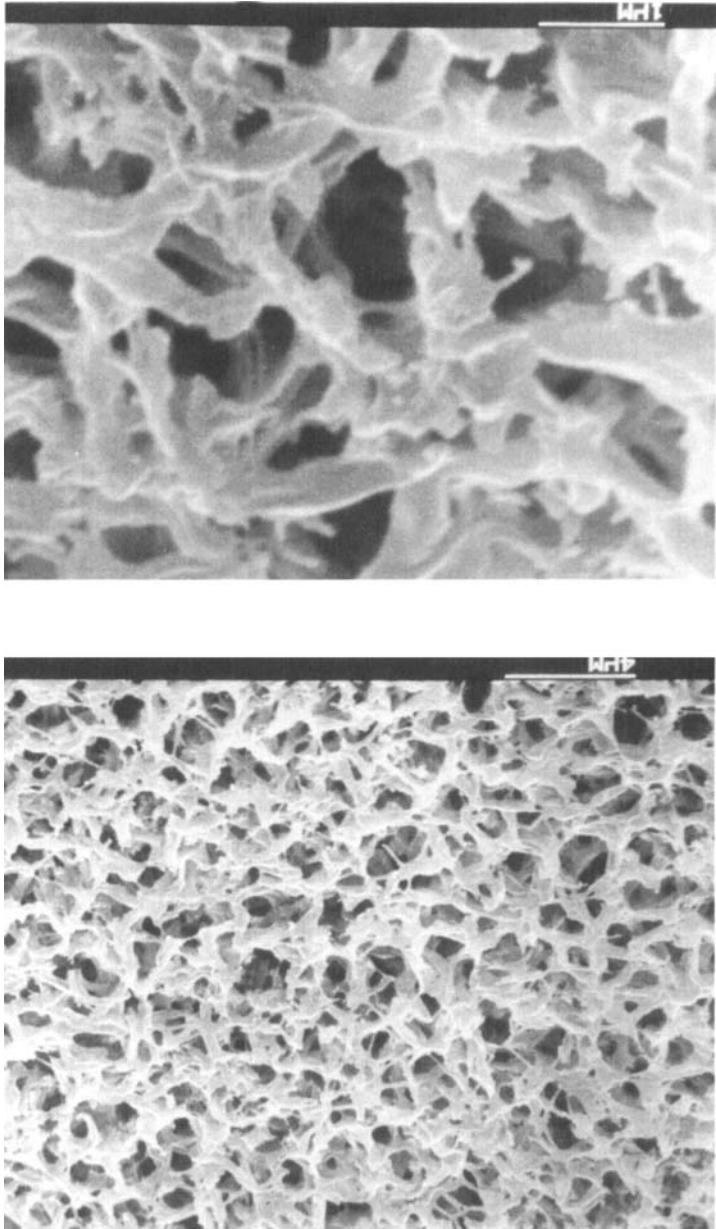


FIG. 2. Scanning electron micrographs of the surface of nylon 66 membrane.

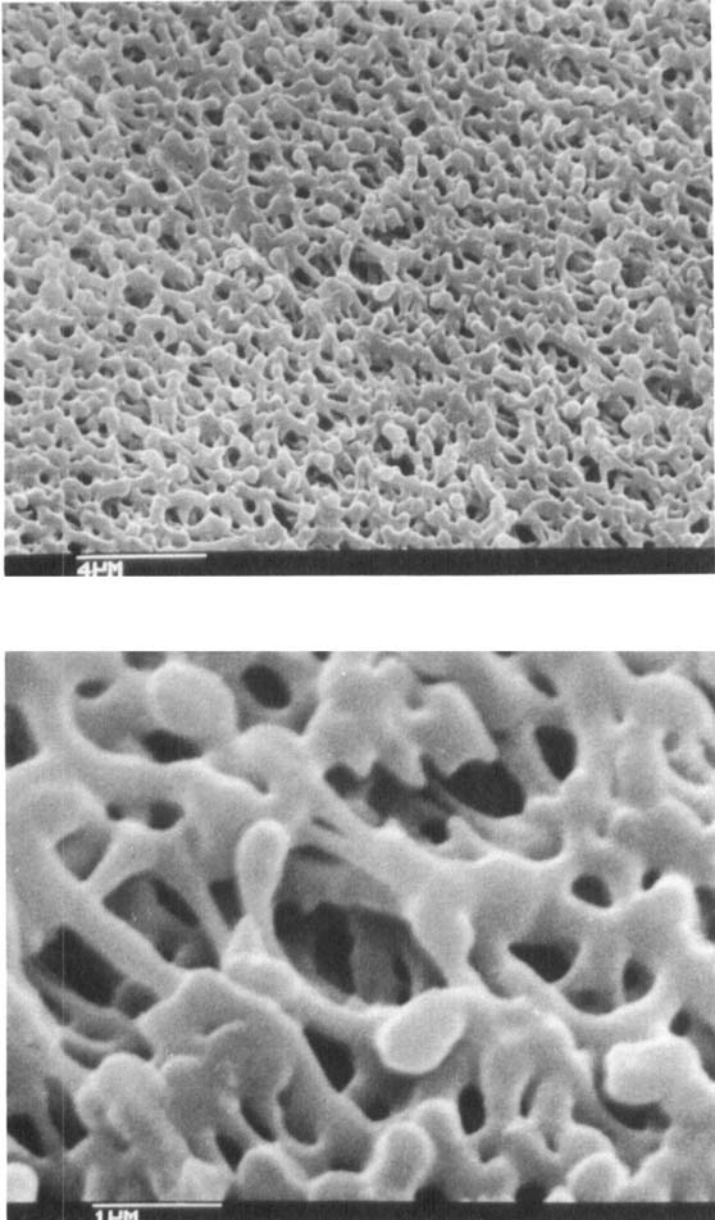


FIG. 3. Scanning electron micrographs of the surface of polysulfone membrane.

TABLE 1
Pore Radii Obtained by Different Methods

Method	Mean radius (nm)		Maximum radius (nm)		Minimum radius (nm)	
	Ny	PSF	Ny	PSF	Ny	PSF
PK	410	420	—	—	—	—
MI	300	250	4100	2800	14	39
LDP	230	180	2600	1480	150	131

CONCLUSIONS

Different methods used to determine pore size and distribution in microfiltration membranes supply different results. The Poiseuille–Knudsen method gives mean radius values which vary up to about 100% from the ones supplied by the manufacturers. The values obtained by the mercury intrusion method are also not comparable with manufacturer’s data. The limit of this method is that the pore structure can collapse and be modified under pressure. Scanning electron microscopy allows only an approximate

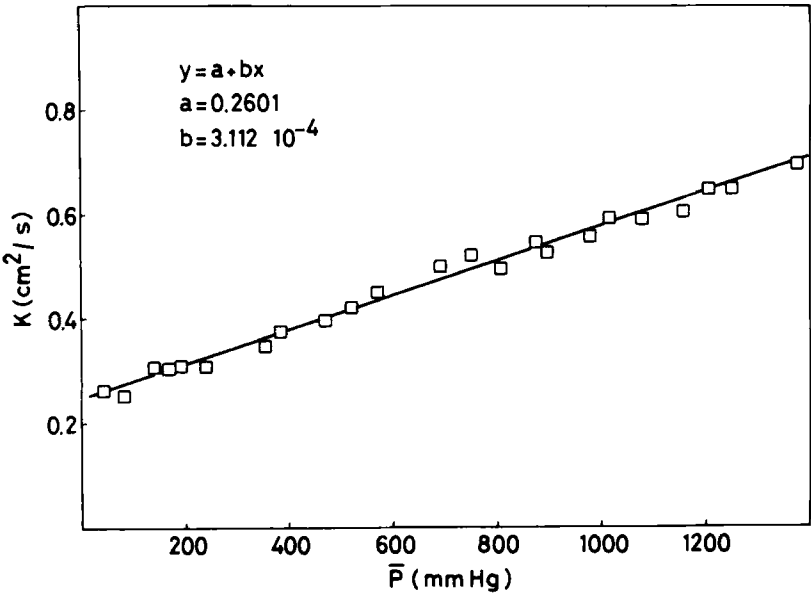


FIG. 4. Relationship between permeability coefficient, K , and mean pressure, \bar{P} , for nylon 66 membrane (Poiseuille–Knudsen method).

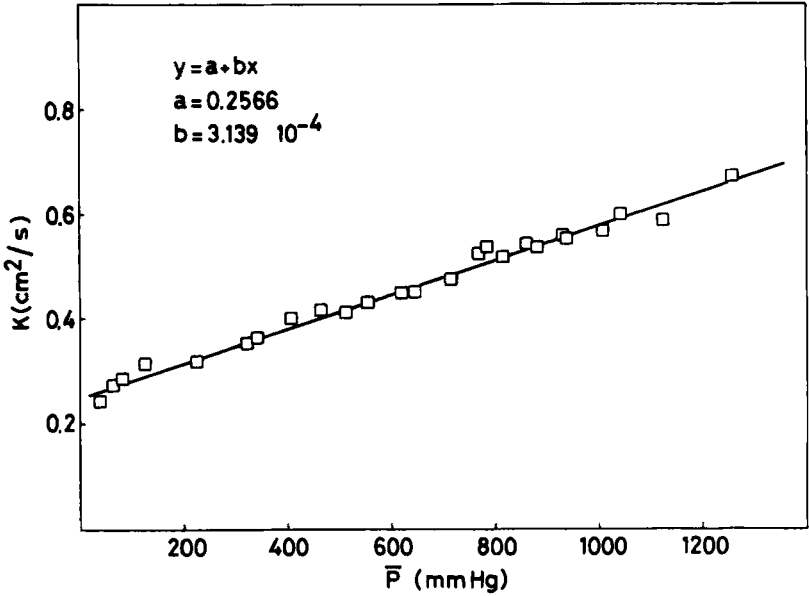


FIG. 5. Relationship between permeability coefficient, K , and mean pressure, \bar{P} , for polysulfone membrane (Poiseuille–Knudsen method).

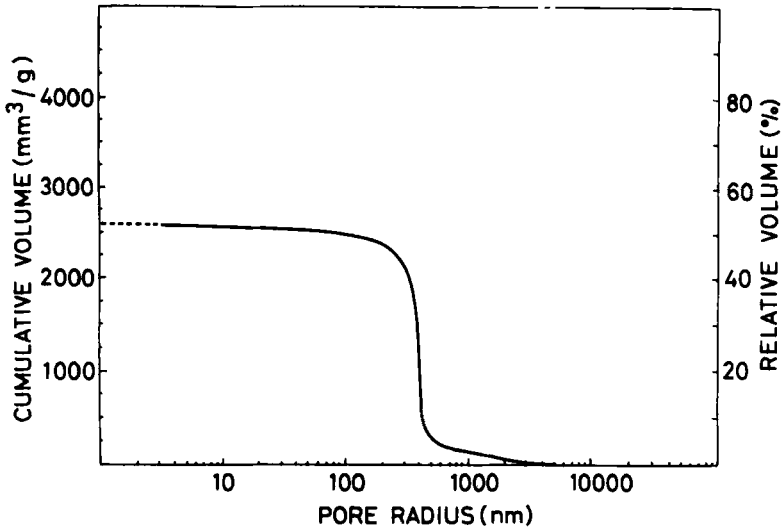


FIG. 6. Pore radius distribution for nylon 66 membrane (mercury intrusion method).

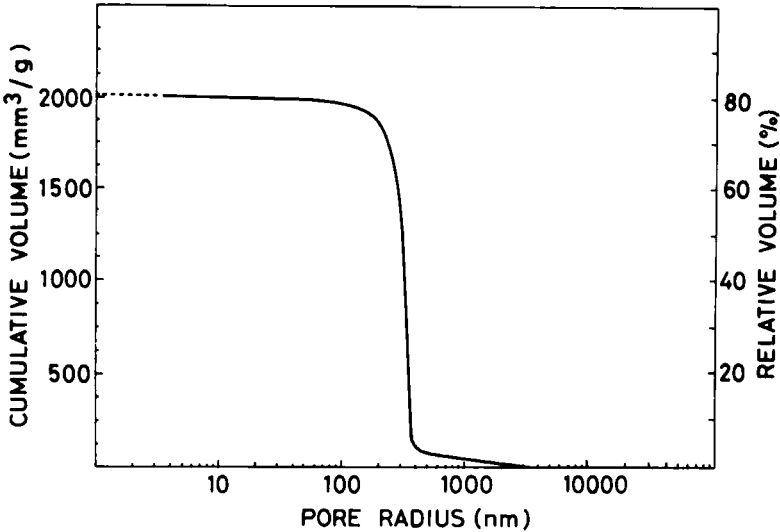


FIG. 7. Pore radius distribution for polysulfone membrane (mercury intrusion method).

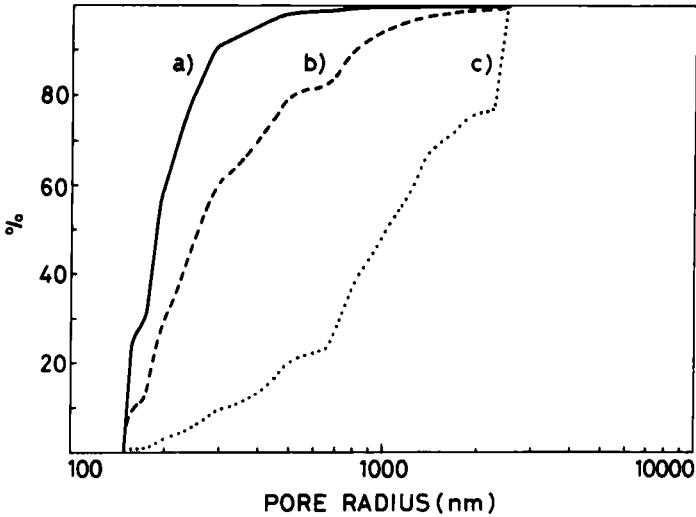


FIG. 8. Percent pores number (a), % pores area (b), and % pores permeability (c) vs pore radius for nylon 66 membrane (liquid displacement porometry).

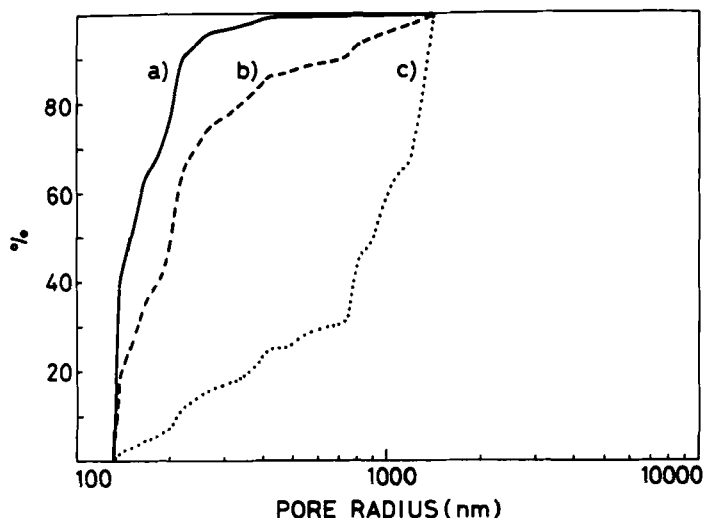


FIG. 9. Percent pores number (a), % pores area (b), and % pores permeability (c) vs pore radius for polysulfone membrane (liquid displacement porometry).

appraisal of pore size distribution. Liquid displacement porometry seems to be the most useful method of investigation. It does not cause alteration in the polymer structure, and it supplies complete and reliable information.

Acknowledgments

This work was financially supported by Ministero dell'Università e della Ricerca Scientifica e Tecnologica (quota 40%) and by Consiglio Nazionale delle Ricerche (Progetto Finalizzato Chimica Fine), Rome, Italy.

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Received by editor November 1, 1990