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# Precise small-angle X-ray scattering evaluation of the pore structures in track-etched membranes: Comparison with other convenient evaluation methods ☆

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ABSTRACT

Poly(ethylene terephthalate) (PET)-based track-etched membranes (TMs) with pore sizes ranging from few nanometers to approximately 1 μm are used in various applications in the biological field, and their pore structures are determined by small-angle X-ray scattering (SAXS). These TMs with the nanometer-sized cylindrical pores aligned parallel to the film thickness direction are produced by chemical etching of the track in the PET films irradiated by heavy ions with the sodium hydroxide aqueous solution. It is well known that SAXS allows us to precisely and statistically estimate the pore size and the pore size distribution in the TMs by using the form factor of a cylinder with the extremely long pore length relative to the pore diameter. The results obtained were compared with those estimated with scanning electron microscopy and gas permeability measurements. The result showed that the gas permeability measurement is convenient to evaluate the pore size of TMs within a wide length scale, and the SEM observation is also suited to estimate the pore size, although SEM observation is usually limited above approximately 30 nm.



## 1. Introduction

Polymeric material modification methods based on irradiation with accelerated heavy ions in the 1–10 MeV/u energy range have been used in various industrial applications such as ultrafiltration membranes with micro- and nanometer-sized pores, templates for the synthesis of micro- and nanowires and tubes, and textured surfaces and bodies with special optical properties [1,2]. Ion tracks in polymers irradiated by heavy ions are chemically etched with alkali solutions, resulting in the production of micro- and nanoporous polymeric materials with precisely controlled geometry.

The size and shape of micro- and nanopores are determined by the ratio of the track etch rate (*Vt*) to the bulk one (*Vb*). The conical pore shape is transformed into a cylindrical one at $Vt \gg Vb$. The *Vb* depends on the material, the etchant composition, and the temperature [1,3]. The *Vt* depends on several factors such as sensitivity of the material to irradiation, irradiation conditions, postirradiation conditions, and etching conditions. In general, the absolute value of *Vt*/*Vb* does not exceed a few tens. However, for poly(ethylene terephthalate) (PET), which is one of the commercially available polymers, this value may be as large as several thousands under controlled postirradiation conditions, leading to the formation of cylindrical pores opening from the front side to the back side of the film in the direction normal to the film surface with the extremely long pore length identical to the film thickness (10 μm–100 μm) [4–7]. The pore diameter can be controlled within a range from 10 nm to 100 μm with the etching time.

These polymeric materials are called "track-etched membranes" (TMs). In addition to the precise determination of pore size with the etching time, the number of pores can be accurately determined with the ion fluence in irradiation of heavy ions. This is advantageous in producing micro- and nanofiltration membranes with adequate properties for practical use. Therefore, the TMs have been applied to process filtration, cell culture, and laboratory filtration in the biological field. In particular, for these applications, it is important to precisely fabricate the pore structure within the range from 10 nm to 1 μm.

In addition, since the separation property of the TMs is highly related to their pore size, a precise and convenient method is

☆ Synopsis: This paper confirms that the gas permeability measurement is convenient for the conventional evaluation of the pore size in the track-etched membranes on the basis of the precise structural characterization by small-angle X-ray scattering.

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required to evaluate the pore size of the TMs. Various evaluation techniques such as scanning electron microscopy (SEM), gas or solvent permeability measurement [8], and conductivity measurement of the etchant during etching have been used for the precise and convenient estimation of pore size. Recently, small-angle X-ray scattering (SAXS) has been used to characterize the pore structures of the TMs for preciseness rather than for convenience [9–12]. It is confirmed that SAXS provides the accurate and statistical structural information on pore size and pore size distribution in the film compared with other evaluation methods.

In this paper, first, we precisely evaluate the pore structures of the TM samples with the pore sizes ranging from few nanometers to approximately 1 μm by SAXS. This evaluation of the pore structures is necessary for the application of TMs in the biological field. Second, we compare the results with those obtained with the other two convenient methods of pore structure evaluation, namely, SEM and gas permeability measurement. Finally, we discuss the choice of the evaluation method for determining the pore size of the TMs.

## 2. Experimental

The PET films already irradiated by Xe ions were purchased from it4ip Co. The film thickness was 12 μm. As-received films were chemically etched with the sodium hydroxide aqueous solution containing 3 wt% sodium hydroxide and 20 wt% ethanol in our laboratory. The etchant was kept at 353 K during the film etching process. The densities of the pores in the films were $7 \times 10^6$ cm$^2$ and $3 \times 10^8$ cm$^2$, which can be determined by the irradiation ion densities. The pore size was controlled by the exposure time to the solution. The samples designated as *A*, *B*, *C*, *D*, *E*, *F*, *G*, *H* and *I* were examined with SAXS for estimating pore diameters and pore size distributions. The sample preparation conditions for all the samples examined in this study are summarized in Table 1.

In this study, we needed to examine the relatively large pore size of approximately 1 μm necessary for industrial applications by SAXS. For this purpose, specially designed apparatuses for SAXS examination were required. The SAXS measurements for characterizing the relatively large pore structures were performed at BL19B2 beamline of SPring-8 (Hyogo, Japan), which is the ultra-small-angle X-ray scattering apparatus equipped with Pilatus 2 M detector and the sample detector distance of 42 m for samples *H* and *I*. The other samples were characterized at our laboratory by using the specially designed SAXS apparatus, which was co-constructed with RIGAKU Corp. for simultaneous measurements of wide-angle X-ray diffraction (WAXD) and SAXS. Pilatus 100 k and 300 k detectors were used for WAXD and SAXS measurements, respectively. The configuration of our laboratory instrument will be described elsewhere.

The cylindrical pore structure with the nanometer-sized diameter and the micrometer-sized length that is identical to the film thickness of 12 μm and is much larger than the pore diameter were analyzed by SAXS. The incident X-rays irradiate the sample from the direction normal to the film surface. In other words, they penetrate the cylindrical pores in the direction parallel to the pore length. In this case, the form factor of the cylindrical pore analyzed can be described with the following form [9,10].

$$F(q,\ R) = 2V\rho_0 \frac{J_1(qR)}{(qR)} \tag{1}$$

here $R$ is the radius of the cylindrical pore, $V$ the volume of the pore and $\rho_0$ the electron density difference between the interior of the pore (air) and the polymer matrix. $J_1$ is the first order Bessel function and $q$ is the magnitude of the scattering vector defined by $q = \frac{4\pi}{\lambda} \sin\theta$ with $\lambda$ and $2\theta$ being the wavelength of the incident X-rays and the scattering angle, respectively. The volume fractions of the pores for all the samples are also included in Table 1, which were estimated to be 0.004%–2.18%, with the pore diameters determined by SAXS and the densities of the pores. Furthermore, Pepy et al. suggest that for a fluence of $3 \times 10^8$ / cm$^2$, only 10% pores are calculated to overlap by using Poisson's law, even for the pores with 310 nm diameter [12]. In this study, the pore size of the samples with the fluence of $3 \times 10^8$ / cm$^2$ is much smaller than 310 nm, and samples *H* and *I* with pore size larger than 310 nm have the fluence two orders of magnitude lower than $3 \times 10^8$ / cm$^2$. This indicates that it is not necessary to consider the structure factor in the SAXS analyses. Therefore, the scattering intensity can be described with the following equation,

$$I(q,\ R) = cF(q,\ R)^2 \tag{2}$$

here $c$ is a constant. Because the sample has pore size distribution, we introduce the pore size distribution into the analytical equation as follows:

$$I(q,\ R_0) = \int_0^\infty I(q,\ R) \cdot \frac{1}{\sqrt{2\pi}\sigma} \exp\left(-\frac{(R-R_0)^2}{2\sigma^2}\right) dR \tag{3}$$

The samples for the SAXS measurements consist of a stack of 10 TM sheets. The exposure time for the SAXS measurements in our laboratory and the synchrotron radiation facility was 60 min and 10 s, respectively. The scattering intensity originated from the

**Table 1**
Sample preparation conditions and pore size and pore size distribution measured by various evaluation techniques.

| Sample | Etching time (min) | Pore density (/cm$^2$) | Volume fraction of the pores (%) | Pore diameter (nm)[a] | Pore diameter (nm)[b] | Pore diameter (nm)[c] | σ (nm)[d] |
|---|---|---|---|---|---|---|---|
| A | 15 | $3 \times 10^8$ | $1.91 \times 10^{-2}$ | 8 (1) | NA | 9.0 (0.5) | 2.0 (0.5) |
| B | 21 | $3 \times 10^8$ | $8.05 \times 10^{-2}$ | 20 (2) | NA | 18.5 (0.5) | 4.0 (0.5) |
| C | 30 | $3 \times 10^8$ | $1.59 \times 10^{-1}$ | 25 (2) | NA | 26.0 (1.0) | 5.0 (1.0) |
| D | 35 | $7 \times 10^6$ | $4.01 \times 10^{-3}$ | 30 (2) | NA | 27.0 (1.0) | 4.0 (1.0) |
| E | 40 | $7 \times 10^6$ | $5.63 \times 10^{-3}$ | 40 (3) | 32 (6) | 32.0 (1.0) | 4.0 (1.0) |
| F | 45 | $7 \times 10^6$ | $6.35 \times 10^{-3}$ | 45 (2) | 35 (5) | 34.0 (1.0) | 7.0 (1.0) |
| G | 50 | $7 \times 10^6$ | $1.72 \times 10^{-2}$ | 60 (4) | 52 (5) | 56.0 (1.0) | 7.0 (1.0) |
| H | 120 | $7 \times 10^6$ | 0.71 | 270 (15) | 320 (30) | 360.0 (5.0) | 18.0 (3.0) |
| I | 200 | $7 \times 10^6$ | 2.18 | 420 (27) | 560 (32) | 630.0 (10.0) | 25.0 (5.0) |

[a] Gas permeability measurements; the average values of four measurements and the standard deviations in the parentheses.
[b] SEM observations, the averaged pore diameter of five pores and the standard deviations in the parentheses.
[c] SAXS measurements, pore diameters and the standard deviations in the parentheses.
[d] pore size distributions and the standard deviations in the parentheses.