

Light Transmission Technique for Pore Size Measurement in Track-Etched Membranes

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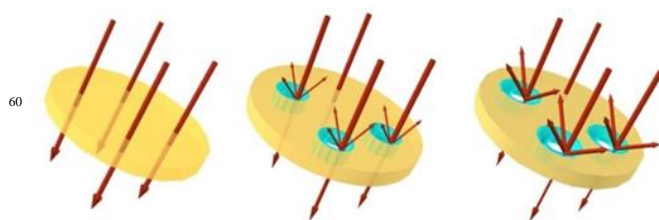
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A new approach is proposed for accurate measurements of the pore sizes in track-etched PET membrane (Polyethylene terephthalate) from nanometer scale to submicrometer scale, which only entailed UV-Vis spectrometry.

Since the discovery of track-etched technology in the late 1960s,¹ filter membranes with needed diameter have found application potential in various fields including food safety,² Environmental pollution,³ biology,⁴ medicine,⁵ fuel cell,⁶ and chemistry.⁷ These track-etched membranes are typically made in polymer membrane through track-etching procedure,¹ during which the polymer membrane is first irradiated by heavy ion beam to form tracks and then cylindrical pores or asymmetric pores are created along the track after wet etching. As important as fabrication of the filter membranes with proper diameters, characterizations and measurements of these materials are of the same paramount. Until now, a few of methods has been developed, which can be classified into the following categories according to the physical mechanisms they exploited: Imaging methods such as Scanning Electron Microscopy (SEM),⁸ Transmission Electron Microscopy (TEM),⁹ Atomic Force Microscopy (AFM);¹⁰ Fluid transports such as Bubble Point¹¹ and Gas Transport;¹² Fluid adsorptions such as Nitrogen Adsorption/Desorption (BEH),¹³ Mercury Porosimetry,¹⁴ Liquid-Vapor Equilibrium (BJH),¹⁵ Gas-Liquid Equilibrium (Permoporometry)¹⁶ and Liquid-Solid Equilibrium (Thermoporometry);¹⁷ Electronic Conductance;¹⁸ Ultrasonic Spectroscopy;¹⁹ Molecular Transport.²⁰ As for imaging methods including SEM and TEM, they entail complex operation procedures which are time-consuming and tedious, precluding those application in large-scale production of filter membrane. Among all these pore size measuring techniques, electronic conductance is the most likely to be used as membrane quality control because of its easiness, repeatability, rapidly and reliability.¹⁸ Nevertheless, the surface charge in the nanopore can lead to the overestimation of the real value, especially when the pore size is decreased to certain value close to the ionic double layer.

Here, we proposed a simple method for quantitative measurement of the pore size formed in track-etched PET membrane (Polyethylene terephthalate), which only entailed UV-Vis spectrometry. PET membrane irradiated by heavy metal ion with ion density of 5×10^7 tracks/cm² is fully transparent and it shows strong absorption below 300 nm. Upon addition of membrane into etching solution, the tracks in PET membrane gradually evolved into cylindrically shaped nanochannels. With prolonged etching time, the membrane

became opaque and semitransparent because surface roughness led to the decrease of light transmission and the enhancement of light scattering and diffraction (Scheme 1 and Fig. S1).



Scheme 1. Schematic illustration of light transmission technique for measuring pore size. The intensity of light scattering increases with the pore size (from left to right).

SEM images of track-etched PET membranes with various etching times (Fig. S2) reveal that the pore size evolution was time-dependent. In order to verify in this manuscript that the pore diameter has linear relationship with the reflected and scattered light intensity, it is imperative to obtain the relationship between non-transmitted light and etching time. Firstly, we set up the etching time at 10, 20, 30, 40, 50 and 60 minutes, respectively. As can be seen in Fig. S2 and S3, the pore size gradually evolved into more than 900 nm in less than one hour and the pore size change also had good linear relationship versus the etching time without interference of the pore overlap.

Secondly, wavelengths scanned from 250 to 800 nm were to acquire detailed spectrum of each polymer membrane (Fig. 1). For bare PET membrane before wet-chemical etching, the membrane showed strong absorption at wavelengths below approximate 300 nm, which is the reason that wavelengths below 300 nm can be used for UV activation of the membrane. Along with prolonged etching time, the 'absorption values' measured at wavelengths above approximate 300 nm were monotonically increased due to light scattering and reflection. However, absorbance values below 300 nm decreased due to mass loss in PET membrane. The plot of 'absorption value' at wavelength of 600 nm versus etching time shows excellent linear relationship between these two parameters (Fig. S4). Since aromatic rings in PET membrane contributed to the UV light absorption and p-phthalic and ethylene glycol were formed during chemical etching, the 'absorption values' above approximate 300 nm can be solely ascribed to the light scattering and reflection by PET membrane, which led to naked eye observed white color.

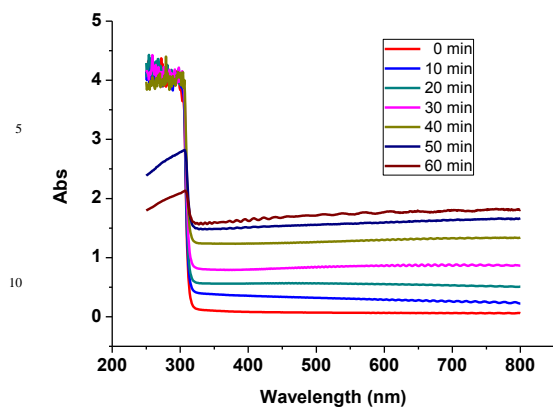


Figure 1. UV/Vis absorption spectra of track-etched PET membranes ($5 \times 10^7/\text{cm}^2$) obtained with different etching time. Measurements were carried out in air. Etching conditions: 2 M NaOH and 65°C .

By plotting the pore size in the membrane versus ‘absorbance value’ at wavelength of 600 nm as shown in Fig. 2, the linear relationship between pore size and ‘absorbance value’ was much superior to the results relying on etching time (Fig. S3.). It has to be noted that all the etching processes were accomplished by one step etching method without any interruption.

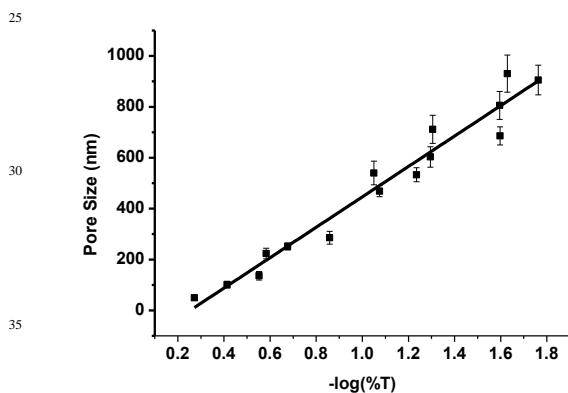


Figure 2. Calibration curve of pore size versus the negative log value of percent transmission of track-etched membranes at wavelength of 600 nm. Data points were derived from three different batches of membrane with track density of 5×10^7 tracks/ cm^2 .

What give rise to the gradually increased light scattering after chemical etching of tracks in the PET membrane? In order to shed light on this phenomenon, we had to find out what kind of physical property related to this polymer membrane had changed during the chemical etching process. Surface roughness has long been considered as a very important factor which contributes to the light scattering property of materials.²¹

The surface of track-etched PET membrane can be divided into three parts (Fig. S5): Part I comprises the surface area located at certain distance D away from the pore in the membrane; Part II comprises the surface areas located between two concentric circles. The first circle is the pore with radius of R , and the second circle has the radius of $R+D$; Part III is defined as the inside surface of the pore in the membrane. The SEM images (Fig. 3 and Fig. S6) clearly show two distinct areas named part I and part II, respectively. The surface area in part II was much brighter than those in Part I,

indicating that different surface morphology or change in the underneath may exist. The above analysis raised one conjecture that the roughness on the surface near the pores and inside the pores played a significant part in scattering and reflecting light instead of the roughness on the surface far away from the pores.

In order to confirm the above reasoning, we have systematically compared PET membranes with different track densities (single, 1×10^4 , 3×10^6 , 5×10^7 tracks/ cm^2). As clearly shown in Figure S7C and D, for membranes with single track and 1×10^4 tracks/ cm^2 , the UV-Vis spectra were nearly not time dependent and had no distinct changes. Whereas the UV-Vis spectra for membranes with track density of 3×10^6 , 5×10^7 tracks/ cm^2 showed the conspicuous increase along with the increase of etching time. Therefore, it can be concluded that the pore evolution in the PET membrane played significant role in the light scattering and reflection, which is highly track-density dependent. In combination with linear fitting of data in Figure S8, the reduction of film thickness only had the negligible effect in the light scattering. Whatever happened beneath the surface far away from pore location should not be taken into account when application of this technique for pore size below $1\mu\text{m}$. Along with the structure underneath the surface close and inside the pore, the surface roughness area near the pore and the inside of the pore were indispensable for our proposed light transmission technique.

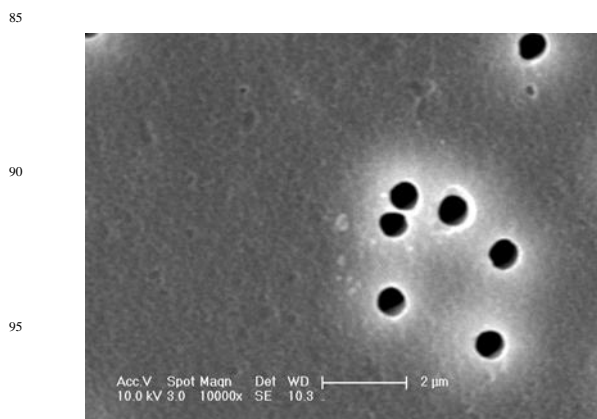


Figure 3. SEM analysis of pore in PET membrane with pore density of 3×10^6 tracks/ cm^2 . White area represents electron accumulated area.

It has been observed that with prolonged etching time for membranes, the part II surface area became bigger and brighter under the same imaging conditions (Fig. S6). Consequently, the overall surface roughness of the PET membrane should also be dependent on etching time. This observation was further validated by qualitative analysis of the surface of PET membrane via AFM. Fig. 4A-E depict the AFM analysis of the PET membrane with track density of 5×10^7 tracks/ cm^2 . It was inspiring to note that the overall average surface roughness (R_a) changed from 3.19 nm to 14.78 nm. In combination of each line profile, the pore evolution was clearly observed. The plot of average surface roughness (R_a) had excellent linear relationship with the etching time (Fig. 4F), which is the prerequisite for the measurement of pore size via light transmission technique.

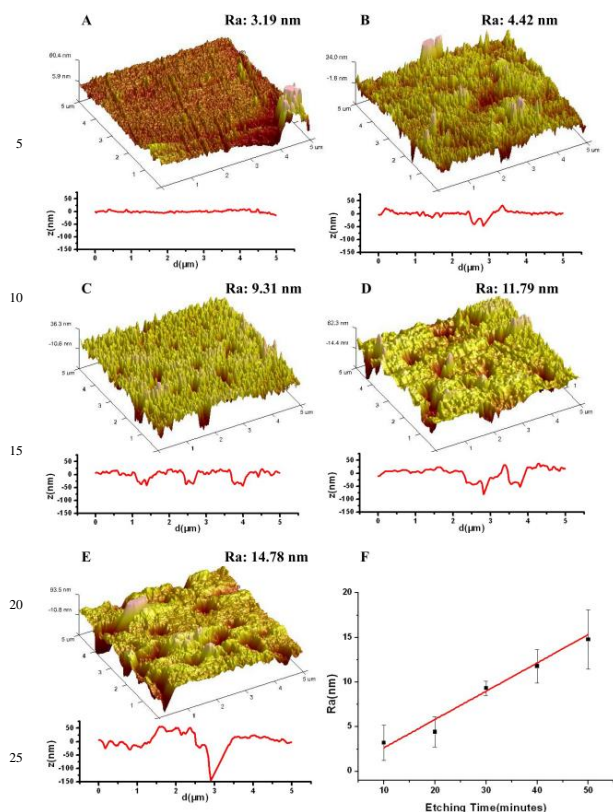


Figure 4. AFM analysis of track-etched PET membranes. From A to E images, the etching times for PET membrane with track density of 5×10^7 tracks/cm² are 10, 20, 30, 40 and 50 minutes, respectively. On the bottom of each image, representative line profiles are reported. (F) Plot of average surface roughness (R_a) versus etching time.

In this study, we proposed a light transmission technique for quantitatively measurement of the pore size embedded in track-etched PET membrane, which only entailed UV-Vis spectrometry. The pore size from nanometer scale to submicrometer scale showed good linear relationship with the negative log value of percent transmit (%T). Although this study mainly focused on the pore sizes located from the scale above 60 nanometers to the submicron scale, there is still sufficient margin for measuring pore size smaller than 60 nm when utilization of light transmission technology proposed herein is in combination with other nano-scale measurement technologies such as Replica Technique and Mercury Porosimetry. With regard to the achievement of this new technology, the application fields can span ultrafiltration and microfiltration based on PET and PC membrane. The light transmission technique proposed herein demonstrated much more reproducibility, easiness, linearity and reliability, which holds great potential in integration with on-line monitoring of pore size evolution.

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Notes and references

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- (a) R. L. Fleischer, P. B. Price and E. M. Symes, *Science*, 1964, **143**, 249; (b) R. L. Fleischer, P. B. Price and R. M. Walker, *Nuclear Tracks in Solids: Principles and Applications*, University of California Press, Berkeley CA, 1975.
 - A. Namvar, I. Haq, M. Shields, K. K. Amoako and K. Warriner, *Food Control*, 2013, **32**, 632.
 - (a) O. Bolormaa, J. Baasansuren, K. Kawasaki, M. Watanabe and T. Hattori, *Nucl. Instrum. Methods Phys. Res. Sect. B-Beam Interactions with Materials and Atoms*, 2006, **243**, 161; (b) L. M. Molodkina, D. D. Kolosova, E. I. Leonova, M. F. Kudoyarov, M. Y. Patrova and Y. V. Vedmetsskii, *Petrol. Chem.*, 2012, **52**, 487.
 - C. D. Lytle, L. B. Routsom, N. B. Jain, M. R. Myers and B. L. Green, *Appl. Environ. Microb.*, 1999, **65**, 2773.
 - R. S. Mazenko, F. Rieders and J. D. Brewster, *J. Microb. Meth.*, 1999, **36**, 157.
 - Y. K. Vijay, M. Dhayal, K. Awasthi, V. Kulshrestha, N. K. Acharya and J. S. Choi, *J. Biomed. Nanotechnol.*, 2006, **2**, 144.
 - D. Fink, I. Klinkovich, O. Bukelman, R. S. Marks, A. Kiv, D. Fuks and W. R. Fahrner, *Biosens. Bioelectron.*, 2009, **24**, 2702.
 - (a) D. Cokeliler, *Appl. Surf. Sci.*, 2013, **268**, 28-36; (b) O. L. Orelovich, B. A. Sartowska, A. Presz, P. Yu. Apel, *J. Microsc.* 2010, **237**, 404.
 - (a) S. Prakash, M. Pinti and K. Bellman, *J. Micromech. Microeng.*, 2012, **22**, 067002; (b) A. H. Colby, Y. L. Colson and M. W. Grinstaff, *Nanoscale*, 2013, **5**, 3496; (c) S. Harrer, P. S. Waggoner, B. Luan, A. Afzali-Ardakani, D. L. Goldfarb, H. Peng, G. Martyna, S. M. Rosnagel and G. A. Stolovitzky, *Nanotechnol.*, 2011, **22**, 275304; (d) C. J. Russo and J. A. Golovchenko, *Proc. Natl. Acad. Sci. U. S. A.*, 2012, **109**, 5953.
 - M. K. Sharma, A. S. Amboliar and S. K. Aggarwal, *J. Nanopart. Res.*, 2012, **14**, 1.
 - K. Nakai, *Membrane*, 2010, **35**, 205.
 - H. Yasuda, J. T. Tsai, *J. Appl. Polym. Sci.* 1974, **18**, 805.
 - Y. Qiao, S.-J. Bao, C. M. Li, X.-Q. Cui, Z.-S. Lu and J. Guo, *Acc Nano*, 2008, **2**, 113.
 - A. Agarwal, A. K. Pandey, S. Das, M. K. Sharma, D. Pattyn, P. Ares and A. Goswami, *J. Membrane Sci.*, 2012, **415**, 60815.
 - F. Casanova, C. E. Chiang, C.-P. Li, I. V. Roshchin, A. M. Ruminski, M. J. Sailor and I. K. Schuller, *Nanotechnol.*, 2008, **19**, 315709.
 - A. Y. Tremblay, C. M. Tam, M. D. Guiver and M. M. Dalcin, *Can. J. Chem. Eng.*, 1991, **69**, 1348.
 - A. Endo, T. Yamamoto, Y. Inagi, K. Wakabe and T. Ohmori, *J. Phys. Chem. C*, 2008, **112**, 9034.
 - (a) N. C. Li, S. F. Yu, C. C. Harrell and C. R. Martin, *Anal. Chem.*, 2004, **76**, 2025; (b) W. Guo, Y. Tian, L. Jiang, *Acc. of Chem. Res.*, 10.1021/ar400024p.
 - T. E. Gómez Álvarez-Arenas, *J. Membrane Sci.*, 2003, **213**, 195.
 - (a) P. Kohli, M. Wirtz and C. R. Martin, *Electroanal.*, 2004, **16**, 9; (b) L. T. Sexton, L. P. Horne and C. R. Martin, *Mol. Biosyst.*, 2007, **3**, 667; (c) P. Kohli, C. C. Harrell, Z. H. Cao, R. Gasparac, W. H. Tan and C. R. Martin, *Science*, 2004, **305**, 984.
 - (a) M. Karamehmedovic, P.-E. Hansen, K. Dirscherl, E. Karamehmedovic and T. Wriedt, *Opt. Express*, 2012, **20**, 21678; (b) A. B. Christiansen, J. Clausen, N. A. Mortensen and A. Kristensen, *Appl. Phys. Lett.*, 2012, **101**, 131902; (c) T. Herffurth, S. Schroeder, M. Trost, A. Duparre and A. Tuennermann, *Appl. Opt.*, 2013, **52**, 3279; (d) S. Muller, C. Scho, O. Picht, W. Sigle, P. Kopold, M. Rauber, *Cryst. Growth Des.* 2012, **12**, 615; (e) M. Pevarnik, K. Healy, M. E. Toimil-Molares, A. Morrison, S. E. Le tant, Z. S. Siwy, *ACS Nano* 2012, **6**, 1757.