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Radiation effects of swift heavy ions in polymers: Determination of nanoshapes from electro-conductivity

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ABSTRACT

The shape of ion track nanopores in polymers depends on the radial distribution of radiation effects. While chain scission dominates in the track core ($r < 5$ nm), cross linking dominates in the track halo ($5 < r < 50$ nm). Therefore, compared with the pristine material, the track core etches at an increased speed, while the track halo etches at a reduced speed. The counteracting effects thus lead to a pore profile that differs from the idealised double-cone profile. We describe an algorithm for retrofitting the pore profile from electro-conductivity data. The technique is supported by field emission SEM in polyethylene terephthalate (PET) and polycarbonate (PC). The results are relevant to biomedical and sensing applications of "conical" and "doubly-conical" nanopores.

1. Introduction

Nanopores produced by etching heavy ion tracks are widely used in contemporary science and technology [1–3]. Conical and doubly-conical nanopores have attracted special interest in the past decade due to their potential in modern and rapidly growing fields, including molecular sensors, logic gates, nanoactuators, and other nanofluidic devices [4–8]. Special interest is focused on single nanopores because they may constitute a unique device for molecular recognition. A significant body of work has been completed on asymmetrical pores obtained via one-sided chemical etching of ion-irradiated polymer foils. These studies have found that such nanopores are approximately conical in shape and possess ionic selectivity and diode-like voltage–current characteristics in electrolyte solutions. It has also been demonstrated that the resistive-pulse sensing of a molecular analyte can be accomplished using the asymmetrical pore. In this case, the pore tip serves as a critical aperture, sensing the passage or adsorption of the analyte. For these applications, the size and shape of the narrowest part of the pore are of primary importance.

In most previous studies, asymmetrical pores were assumed to be conical. The large diameter of the conical pore can be determined using electron microscopy. In contrast, it is practically impossible to image the narrow end (tip) of a single nanopore; thus, estimates of the pore tip diameter are always based on the measured electrical conductivity. The relation between the electrical conductivity, G, of a pore filled with a solution of specific conductivity, k, and the geometrical parameters is expressed by the formula

$$G^{-1} = \frac{1}{\pi k}\int_0^L \frac{dx}{r_x^2} \tag{1}$$

Here, L is the pore length and r_x is the radius along the pore axis x. In the special case of the cone, whether single or double, formula (1) leads to the simple equation:

$$G = \frac{k\pi dD}{4L} \tag{2}$$

where d and D are the diameters of the small and large bases, respectively. This approach was initially suggested as a rough approximation [4]; however, over the past decade, it has been widely used to determine the effective tip diameter. Considerable information on the conductive, selective, chemical, electrical and other properties of asymmetrical pores has been accumulated. Despite these efforts, a striking imbalance remains between the

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extensive knowledge about the electrical properties of the pore and the superficial knowledge about its geometry.

A closer inspection of the geometry of the so-called conical pores is the goal of this work. To date, the necessity of this subject has been overlooked, though the conical geometry is no more than a macroscopic model. On the nanoscale, the shape of a track-etched pore should reflect the latent track structure [3]. A latent track of heavy ions in polymer consists of two zones with different etching behaviours. The track core is highly damaged and etches at high speed, and its diameter is approximately 5–10 nm. The track halo is a cross-linked zone that starts at a diameter of 5–10 nm and ends at a diameter of 50–100 nm. Due to cross-linking, the etching rate in the track halo is reduced with respect to the bulk etching rate [9]. This inevitably affects the pore shape at small diameters (<100 nm) and leads to an "elongation" of the tip, i.e., a deviation from the conical shape. In this paper, we present a quantitative analysis of the pore shape from conductometry and estimate the influence of the latent track structure on the longitudinal profile of the so-called "doubly-conical" and "conical" pores.

2. Experimental section

2.1. Polymer foils

Polyethylene terephthalate biaxially oriented foils (10 μm thick PET, GOST-24234-80, USSR, and 12 μm thick Hostaphan RN, Kalle, Germany) and polycarbonate (PC) foils (Makrofol N, Bayer, Germany, 30 μm thick) were used.

2.2. Ion irradiation

The foil samples were irradiated with single 11.4 MeV/u Xe, U and Au ions at the UNILAC facility of GSI (Darmstadt). Reference samples were irradiated with the same ions, at 11.1 MeV/u energy, and at fluences of 10^7–10^8 cm^{-2}. Stacks consisting of 4–10 samples were exposed at normal incidence. Irradiations with single 1.2 MeV/u Xe ions and many 1.2 MeV/u Kr ions were also performed using the IC-100 cyclotron (FLNR JINR, Dubna).

2.3. Etching and measurement conditions

Etching of single- and multi-track samples was performed in the same compression-sealed two-compartment electrolytic cell to provide identical treatment conditions. Both halves of the cell were charged with 9 M NaOH. The foil thickness was measured before and after etching, and its average thickness was used to determine the bulk etch rate. High alkali concentration was used to ensure the fabrication of "conical" pores by maintaining a relatively low track-to-bulk etch rate ratio. Conductometric monitoring of the etching process for single-track samples was performed using a PC-controlled RCL-meter (HIOKI instrument, model 5322). After filling both compartments with the etchant, the electrical resistance was measured by applying a sine voltage with an amplitude of 0.5 V and a frequency of 1333 Hz to the gold electrodes [10]. Pore breakthrough was characterised by a sharp onset of the electrical current. Electron microscopy investigations were performed on multi-track samples. These reference samples containing many ion tracks were etched under identical concentrations and temperatures. After etching, the samples were examined using an LEO 1530 field and a Carl Zeiss Ultra Plus field emission scanning electron microscope. Embrittled samples were fractured to observe the inner pore structure. Details of the sample preparation and FESEM examination have been reported previously [10,11].

3. Results and discussion

Analysis of the electrical conductance measured during etching provides valuable information about the growing nanopore. Experimentally measured curves, $G^{1/2}(t)$, for different bombarding ions are shown in Fig. 1. Each curve has two inflection points appearing within the first 20 min after breakthrough. To explain the shape of the experimental curves, a doubly-conical pore is considered the simplest model (Fig. 2a). According to the double-cone model, two circular cones form symmetric to the centre plane of the foil and advance towards each other at the track etch speed V_T [1]. The bulk etching of the material is characterised by the bulk etch speed, V_B. After breakthrough ($t > t_b$), the pore has the geometry of two truncated cones with a cone base diameter, D, and a constriction diameter, d. Based on Eq. (2), the pore conductivity, G, as a function of time can be written as follows [11]:

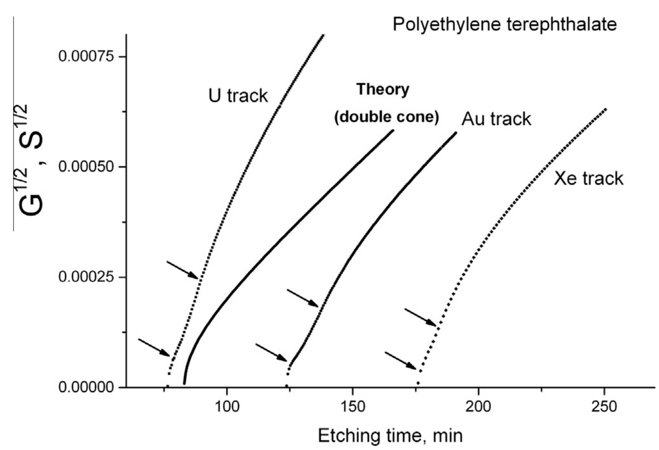

Fig. 1. The square root of pore conductance as a function of etching time for single tracks of U, Au and Xe ions in PET foil. The theoretical curve calculated by formula (3) is shown for comparison. Arrows indicate inflection points on the experimental curves. Etching conditions: 9 M NaOH, room temperature.

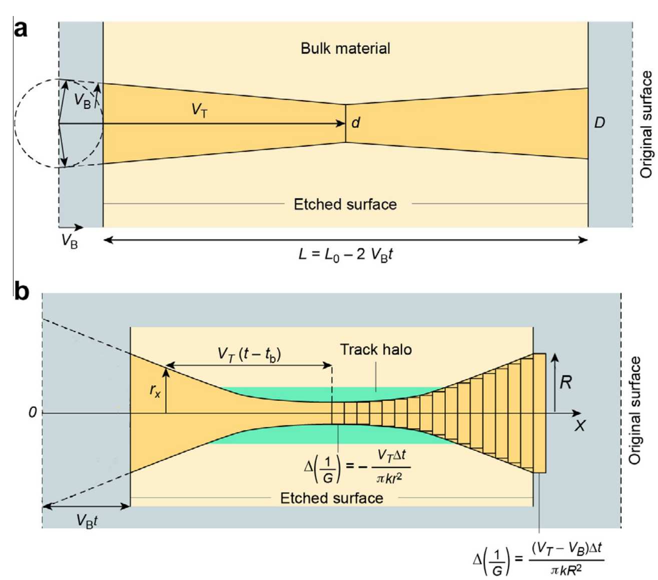

Fig. 2. Two models for two-sided ion track etching: (a) Double-cone. (b) Funnel-like model considers the reduced etching rate in the latent track halo. The right-hand half of the pore is divided into thin slices to illustrate the principle used to calculate the pore profile from the pore resistance. After each time step, Δt, the innermost slice annihilates, and a new slice is formed at the surface. The relevant changes in the pore resistance, $\Delta(1/G)$, are shown. For other designations, see the text.