Available online at www.sciencedirect.com
ScienceDirect
Nuclear Instruments and Methods in Physics Research B 264 (2007) 311–317
NIM B
Beam Interactions with Materials & Atoms
www.elsevier.com/locate/nimb

Synthesis of polymeric micro- and nanostructural materials for application in non-linear optics

Lyubov Kravets [a,*], Natalia Palistrant [b], Valerii Bivol [b], Stepan Robu [b], Nikolai Barba [b], Oleg Orelovitch [a]

[a] Joint Institute for Nuclear Research, Flerov Laboratory of Nuclear Reactions, Joliot-Curie Str. 6, 141980 Dubna, Moscow Region, Russian Federation
[b] Institute of Applied Physics of Moldavian Academy of Sciences, Academiei Str. 5, MD-2028 Chisinau, Moldova

Received 18 April 2007; received in revised form 9 July 2007
Available online 14 September 2007

Abstract

The present paper describes a new approach developed for the preparation of micro- and nanostructural materials on the basis of polymeric compositions used as a matrix in non-linear optics. This approach consists in filling the pores of poly(ethylene terephthalate) track membranes (PET TM) from polymeric compositions using an impregnation method. It is shown that depending on the concentration of polymeric compositions in the solution it is possible to form a variety of micro- and nanostructural materials (tubules and wires as well as composite membranes) with a wide spectrum of characteristics. The developed method of producing micro- and nanostructural materials provides a possible way for creating polymeric objects with non-linear optic properties which can be used to design electronic micro- and nanodevices and to obtain chemical and optical sensors.

PACS: 61.46.Tw

Keywords: Template synthesis; Track membrane; Polymeric compositions; Micro- and nanostructural materials; Non-linear optics

1. Introduction

In recent years the problem of producing micro- and nanostructural materials with porous materials as a template has excited great interest [1,2]. This method consists in filling the pores of the template with a desired material by various physicochemical methods. These investigations are of major practical and scientific importance since they allow obtaining of a wide spectrum of micro- and nanostructural materials with unique properties for application in various areas of modern science and technologies: nanoelectronics, photonics, chemotronics, biotechnologies, etc. Two types of porous membranes: the aluminum membranes and the polymeric track membranes are often used as templates. Aluminum membranes are achieved via anodization of aluminum foil in acid media [3], and the track membranes are produced by an irradiation of polymeric films with a beam of highly energetic heavy ions followed by a subsequent chemical etching of the resulting particle latent tracks [4,5]. Both types of membranes have cylindrical pores with a narrow pore size distribution that gives an opportunity for the synthesis of micro- and nanostructural objects – wires, tubules as well as composite membranes. When the pore area is completely filled by a desired material, micro- and nanowires are produced, if the used material is deposited along the pore walls only, micro- and nanotubules are formed. In order to fill the pores of the template various materials can be used: metals [6–8], carbon [9,10], semiconductors [11,12], polymers [13–15]. The micro- and nanostructures can remain inside the pores of the template or they can be freed from the membrane. To produce free micro- and nanowires as well as free micro- and nanotubules, the porous matrix is dissolved

* Corresponding author. Tel.: +7 49621 62448; fax: +7 49621 28933.
E-mail address: kravets@lnr.jinr.ru (L. Kravets).

0168-583X/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.nimb.2007.09.020

by a suitable solvent and free particles are therefore recovered on a substrate by filtration. If the micro- and nanostructural objects (wires or tubules) are still linked to the surface of the substrate after matrix dissolution, a brush structure can be obtained. The synthesized micro- and nanotubules can be also left inside the pores of the template and composite membranes are then produced. If the tubule inner diameter is around a few nanometers: usually from 1 to 4 nm, a so-called "ion-gated" membrane is therefore formed and its properties can vary under the influence of external factors, such as pH of the solution, electric current and ionic force of the solution [16–18].

One of the ways to obtain micro- and nanostructures using porous membranes as templates is the electrolytic deposition. This method is used for the synthesis of micro- and nanowires as well as micro- and nanotubules from metals. Another way is related to the chemical or electrochemical polymerization of monomers. This looks more promising as it allows to use a wide variety of organic compounds and to obtain a micro- or nanostructural composite material that often possess unique properties, as e.g. polymers with electric conducting properties [19–21]. More recently, the method of obtaining nanomembranes by polymerization of monomer vapors in plasma has been more and more often used [22,23]. In our opinion, the use of plasma has a number of advantages such as the possibility to regulate thickness and density of the deposited polymeric layer. It also provides its high adhesion to the template, reduces the synthesis time and gives access to a wider range of organic compounds for which the standard polymerization is impossible.

This paper presents a new approach developed for preparation of micro- and nanostructural materials (wires and tubules as well as composite membranes) from polymeric compositions by filling the pores of a track etched membranes. The used track membranes were developed and serially produced from a poly(ethylene terephthalate) film at the Flerov Laboratory of Nuclear Reactions of the Joint Institute for Nuclear Research. The polymeric compositions were based on styrene, butylmethacrylate and 4-aminostyrene, the impregnation method was applied for obtaining polymeric micro- and nanostructural materials. We studied the mechanism of formation of these materials as well as their structure and properties. The developed method of producing micro- and nanostructural materials provides a possible way for creation of polymeric objects with non-linear optic properties which can be used to design electronic micro- and nanodevices and to obtain chemical and optical sensors.

2. Experimental

Two types of membrane were used as templates for synthesis of micro- and nanostructural materials: a PET track membranes with a thickness of 10.8 μm and an effective pore diameter of 1.0 μm (pore density was $1.5 \times 10^7\ \mathrm{cm}^{-2}$) and a PET track membrane with a thickness of 19.8 μm and an effective pore diameter of 3.0 μm (pore density was $1.0 \times 10^6\ \mathrm{cm}^{-2}$). In order to produce the membranes, poly(ethylene terephthalate) films (Hostaphan RE5, Kalle) were irradiated by krypton positive ions, accelerated at the energy ~3 MeV/nucleon at the cyclotron of the Flerov Laboratory of Nuclear Reactions. The irradiation is carried out under vacuum of 0.15 Pa at room temperature. The irradiated samples were kept in air under normal conditions. Then the ion irradiated films were additionally sensitized with ultraviolet irradiation from a source with maximum intensity at 310 nm. Chemical etching was performed in an alkaline (NaOH) aqueous solution of 3.0 or 5.0 N at 85 °C for a time up to 6 min. The technique of producing the track membranes is described more detail in [5].

Polymeric compositions were used as a precursor for obtaining micro- and nanostructural materials. These polymeric compositions were prepared by radical copolymerization of styrene and butylmethacrylate in ratio of 50:50 mol% and styrene, butylmethacrylate and 4-aminostyrene in ratio of 20:50:30 mol% as described in [24]. Toluene was used to dissolve the polymeric compositions. The concentration of the polymeric compositions in the solution was varied from 0.5 up to 20%. The membranes were covered by the solution of polymeric compositions using the impregnation device of a "meniscus" type (see the scheme in Fig. 1). The technique of applying of the polymeric compositions on the membrane surface consists in the following. The membrane samples of size 100 mm × 100 mm, as a flexible basis, are fixed on a rotating drum of a diameter of 50 cm. The drum begins its movement with the help of reversible engine. The bath with a solution of the polymeric composition is placed on a horizontal small table under the drum. As far as the bath approaches the drum, the solution is uniformly distributed all over the membrane surface. Then the solvent is subjected to evaporation at room temperature. Full drying of the samples was carried out in free of dust chamber at elevated temperature.

The characteristics of initial membrane and the ones with a deposited layer of the polymeric compositions were determined through a series of complementary procedures. The amount of the polymeric composition on the membrane surface determined by relation

$$Q_g = (m_g - m_o) \cdot 100/m_o,$$

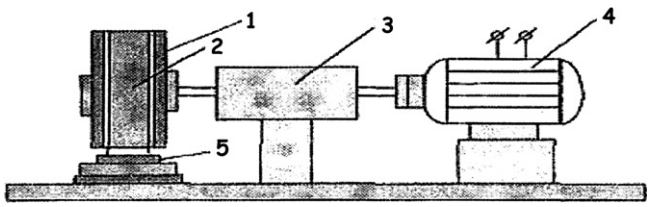

Fig. 1. Scheme of the impregnation device: (1) drum; (2) membrane; (3) reducer; (4) reversible engine; (5) bath with solution of polymeric composition.