Available online at www.sciencedirect.com
SCIENCE DIRECT®

ELSEVIER

Journal of Membrane Science 256 (2005) 64–71

journal of MEMBRANE SCIENCE

www.elsevier.com/locate/memsci

Track etched membranes with thermo-adjustable porosity and separation properties by surface immobilization of poly(*N*-vinylcaprolactam)

W. Lequieu, N.I. Shtanko, F.E. Du Prez [*]

Department of Organic Chemistry, Polymer Chemistry Research Group, Ghent University, Krijgslaan 281 S4-bis, B-9000 Ghent, Belgium

Received 27 October 2004; received in revised form 7 February 2005; accepted 9 February 2005
Available online 13 March 2005

Abstract

The surface of poly(ethylene terephthalate) (PET) track etched membranes (TMs) was covered with thermo-responsive poly(*N*-vinylcaprolactam) (PVCL) by a photochemical immobilization method. First, a photo-reactive azidophenyl group was incorporated into the thermo-responsive PVCL chains. Secondly, the polymers were cast on the PET membrane followed by irradiation with UV light. Characterization by X-ray photoelectron spectroscopy and FT-ATR-IR demonstrated that the thermo-responsive polymer chains are effectively grafted on the membrane surface. Scanning electron microscopy and atomic force microscopy on the dry composite membranes demonstrated that the pore size diameter decreases and the surface roughness increases with increasing amount of grafted polymer chains on the TM. The water permeation through the modified TM drastically increases when the cloud point (T_{cp}) of the grafted PVCL-chains is reached. The permeability of a mixture of dextrane molecules is not only controlled by the molecular weight of the individual macromolecules but also strongly by temperature. This last observation opens the possibility to use the same membranes for the separation of macromolecular mixtures over a broad molecular weight range.

Keywords: Track etched membranes; Thermo-adjustable separation; Poly(*N*-vinylcaprolactam); Lower critical solution temperature; Photochemical immobilization

---

1. Introduction

Polymer track etched membranes (TMs) are thin polymer films with discrete pores that are formed through a combination of heavy ions bombardment and chemical etching [1]. The particle bombardment results in the formation of latent tracks through the films [2,3]. Controlled chemical etching of this modified zone leads to the formation of pores with a defined pore size. By choosing appropriate conditions for irradiation and etching, it is possible to prepare a wide range of polymer TM. The pore size, shape and density can be varied in a controllable manner, which allows for the production of membranes with the required transport and retention characteristics [4]. TM have found diverse applications in biotechnology, medicine, ecology, etc. [1]. Modification of such a membrane by grafting it with polymers extends the possibility of their use [5,6]. Preparation of modified polymer membranes with unique properties, in particular TM with controlled permeability, is of substantial interest.

Many investigations were devoted to obtain membranes with the ability to open and close the pores in response to an external stimulus such as temperature [7–10], pH [11] and ionic strength [12]. A number of investigations have reported the preparation of porous membranes with thermo-responsive poly(*N*-isopropylacrylamide) (PNIPAAM) on the surface and in the pores [7–10]. PNIPAAM and its copolymers made it possible to regulate the permeability in response to the environmental temperature. Poly(*N*-vinylcaprolactam) (PVCL) is another well studied polymer with lower critical solution temperature (LCST) behaviour, which shows a much different response towards temperature as compared to PNIPAAM [13–16]. The actual interest in PVCL is connected with the combination of its thermo-sensitive properties and biocom-

---

[*] Corresponding author. Tel.: +32 9 264 45 03; fax: +32 9 264 49 72.
E-mail address: filip.duprez@ugent.be (F.E. Du Prez).

0376-7388/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.memsci.2005.02.007

patibility [17]. Presently, there are no studies concerning the application of PVCL for surface modification of porous membranes.

In this work, we immobilized thermo-sensitive PVCL copolymers on TM by a photochemical immobilization method that offers an important advantage to other covalent immobilization procedures. The chemistry is independent of the chemical nature of the immobilized polymer and the substrate [18,19]. This immobilization on the surface of poly(ethylene terephthalate) (PET) TM occurs via photosensitive azide-groups that are incorporated in the PVCL chains. The membrane surfaces have been examined with Fourier transform attenuated total-reflectance infrared spectroscopy (FT-ATR-IR), scanning electron microscopy (SEM), atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS).

The permeation of respectively water and dextrane molecules with molecular weight range between 6000 and 2,000,000 through the novel composite membranes have been investigated as a function of temperature.

2. Experimental

2.1. Materials

PET track membranes were kindly donated by the Flerov Laboratory of Nuclear Reactions (Joint Institute for Nuclear Reactions, Dubna, Russia). The TM used have a thickness of 20 μm, pore sizes are 0.1, 0.2 and 0.4 μm and the pore density is 10^8 cm^{-2}. *N*-vinylcaprolactam (VCL; Aldrich 98%) was purified by recrystallization from benzene with further drying under vacuum for 10 h at 35 °C and stored at 4 °C under nitrogen. Acrylic acid (AA; Aldrich 99%) was purified by vacuum distillation at 39 °C at a pressure of 15 mm Hg and stored at 4 °C under nitrogen. Isopropanol (IPA; Lab-Scan 99.8%) was purified by distillation over CaO just before use. 2,2′-Azobisisobutyronitrile (AIBN; Across 98%) was purified by recrystallization from methanol. Dimethylformamide (DMF; Lab-Scan 99.8%), ethanol (Aldrich, HPLC grade), diethyl ether (Lab-Scan 99.8%), 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (WSC, Aldrich 99%), morpholine-4-ethanesulfonic acid hydrate (MES monohydrate; Aldrich 99%), azidoaniline (Aldrich 99%), aniline (Acros, ACS reagens) and dextrane (M_n = 6000, 100,000 and 2,000,000, Fluka Biochemika) were used as received.

2.2. Synthesis of azidophenyl containing poly(N-vinylcaprolactam)

Copolymers of AA and VCL (P(VCL-*co*-AA)) have been prepared by free radical copolymerisation of VCL with AA in the presence of AIBN as initiator. In a typical procedure, 10 g (92.4 mol%) of VCL, 0.3 ml (5.6 mol%) AA and 0.25 g (2 mol%) of AIBN were dissolved in 13.5 ml of isopropanol. The reaction was purged with nitrogen for 15 min and allowed to react in an oil bath at 70 °C for 24 h under nitrogen. After reaction, the solution was dissolved in methanol and precipitated in diethyl ether at low temperature. The precipitation was carried out three times and the product was dried in vacuum at room temperature for 48 h.

For the synthesis of the azidophenyl containing polymer (P(VCL-*co*-AA/Az)), certain amount of P(VCL-*co*-AA) (500mg), 4-azidoaniline (62 mg) and WSC (2 mg/ml) were dissolved in 10^{-4} M MES-buffered solution (50 ml, pH 7.0) and the solution was stirred for 48 h at 4 °C in the absence of light. After the reaction, the solution was subjected to ultrafiltration with track membranes (pore size 0.1 μm), and the polymeric product was washed twice with diluted hydrochloric acid (pH 2) and twice with distilled water. The polymer was stored in wet state at low temperature under nitrogen.

Modification of P(VCL-*co*-AA) with aniline was performed by an analogue procedure whereby 4-azidoaniline was replaced by aniline. The modified P(VCL-*co*-AA/An) polymers were purified by triple precipitation in diethyl ether followed by drying in vacuum at room temperature.

2.3. Surface immobilization of P(VCL-co-AA/AZ)

Certain amount of P(VCL-*co*-AA/Az) was dissolved in DMF (concentration between 2 and 10 wt.%) and was cast on PET TMs. After drying at room temperature, the TM were placed for 20 min under a 900 W 400-L UV lamp (16 mW/cm^2) with an emission maximum at 365 nm. After irradiation, the TM were extracted with ethanol and distilled water for 48 h for the removal of non-attached polymer. The final PVCL-amount on the membranes is controlled by the initial copolymer concentration and the number of times that the photo-grafting procedure has been performed (between one and three times). The degree of grafting (Q_{gr}) was determined gravimetrically and calculated according:

$$Q_{gr}\,(\%) = \frac{W_1 - W_0}{W_0} \times 100 \qquad (1)$$

where W_0 and W_1 respectively denote the mass of the membrane before and after the grafting process.

2.4. Instruments

The molecular weight (M_n) and the molecular weight distribution (M_w/M_n) of the copolymers were measured with a 60 cm mixed-C DL-gel 5μ column (Polymer Laboratories) on a waters gel permeation chromatography (GPC) instrument equipped with Waters 2400 RI detector with “Millenium” software. DMF was used as eluent at a flow rate of 0.5 ml/min. The GPC-system was calibrated with polystyrene standards. Copolymer composition determined by titration according to a procedure described earlier [20].

The cloud point of the polymer was determined with the turbidimetric method. The transmittance for each polymer sample, equilibrated with water in a test tube, was measured with an UV–vis spectrophotometer (Kontron instruments,