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Materials Chemistry and Physics 94 (2005) 195–201
MATERIALS CHEMISTRY AND PHYSICS
www.elsevier.com/locate/matchemphys

Fluorinated polyimides grafted with poly(ethylene glycol) side chains by the RAFT-mediated process and their membranes

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Received 8 January 2005; received in revised form 17 March 2005; accepted 13 April 2005

Abstract

Graft polymerization of poly(ethylene glycol) methyl ether methacrylate (PEGMA) from fluorinated polyimide (FPI) was carried out by the reversible addition-fragmentation chain transfer (RAFT)-mediated process. The peroxides generated by the ozone treatment on FPI facilitated the thermally-initiated graft copolymerization from FPI backbone. The "living" character of the graft chain growing was ascertained in the subsequent chain extension of PEGMA. Nuclear magnetic resonance (NMR) and molecular weight measurements were used to characterize the chemical composition and structure of the copolymers. Microfiltration (MF) membranes were fabricated from the FPI-*g*-PEGMA comb copolymers by phase inversion in aqueous media. Surface composition analysis of the membranes scanned by X-ray photoelectron spectroscopy (XPS) revealed a substantial surface enrichment of the hydrophilic components. The pore size distribution of the resulting membranes was found to be much more uniform than that of the corresponding membranes cast from FPI-*g*-PEGMA prepared by the conventional radical polymerization process in the absence of the chain transfer agent. The morphology of the membranes was characterized by scanning electron microscopy (SEM).

Keywords: Polymer materials; Polyimide; Membrane; RAFT; Pore size

1. Introduction

The polyimide (PI) membranes are widely used in microfiltration (MF) and ultrafiltration (UF) due to their excellent processability, chemical resistance, well-controlled porosity, and good thermal property [1]. Several approaches have been developed to endow the conventional hydrophobic membranes with hydrophilic properties. These approaches have included coating and grafting techniques. In the former approach, the membranes are dipped in solutions containing the hydrophilic polymers [2,3]. The approach of molecular or bulk graft copolymerization of a functional (hydrophilic) monomer with a hydrophobic polymer, followed by phase inversion in an aqueous medium, to membrane fabrication may prove to be particularly useful in certain cases [4–6]. Graft copolymerization via the conventional free-radical process usually leads to uncontrolled size distribution of the graft chains. Graft copolymerization by the reversible addition-fragmentation chain transfer (RAFT)-mediated process, however, can be expected to produce well-defined side chains, which, in turn, can be expected to improve the uniformity in pore-size distribution of the membrane during the phase inversion process.

The synthesis of graft copolymers based on commercial polymers is most commonly accomplished via the free-radical process. Free-radicals are produced on the parent polymer chains by exposure to ionizing radiation, and/or a free-radical initiator [7–9]. Alternatively, peroxide groups are introduced onto the parent polymer by ozone pretreatment to serve as the initiation sites for the free-radical polymerization of a monomer [10–14].

In the present work, fluorinated polyimide (FPI) grafted with poly(ethylene glycol) methyl ether methacrylate

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doi:10.1016/j.matchemphys.2005.04.017

(PEGMA) (FPI-*g*-PEGMA) copolymers are synthesized by living radical graft polymerization of PEGMA with ozone-pretreated FPI under the RAFT-mediated process. MF membranes are fabricated from FPI-*g*-PEGMA comb copolymers by phase inversion in aqueous media. Well-defined pore size and pore size distribution of the resulting membranes are confirmed by morphology observation. Anti-fouling property of the hydrophilic MF membranes is found by determination of surface composition.

2. Experimental

2.1. Materials

The fluorinated polyimide (FPI) used in this study was prepared from step polymerization of 2,2-bis(3,4-dicarboxyphenyl) hexafluoropropane dianhydride (6FDA) and 4,4′-bis(4-aminophenoxy) diphenyl sulfone (BADS) according to the method reported previously [15]. The macromonomer, poly(ethylene glycol) methyl ether methacrylate ($\bar{M}_n = 300\,\mathrm{g\,mol^{-1}}$), was purchased from Aldrich Chemical Co., and was used after removal of the inhibitor in an Al_2O_3 column. The solvent, *N*,*N*-dimethylformamide (DMF), was purchased from Fisher Scientific Co., Leics, UK, and was used as received. The chain transfer agent (CTA), 1-phenylethyl dithiobenzoate (PDB), was prepared according to the published procedures [16,17].

2.2. Preparation of FPI-g-PEGMA copolymer via RAFT-mediated process

The FPI powders were dissolved in DMF to a concentration of $75\,\mathrm{g\,L^{-1}}$. A continuous stream of O_3/O_2 mixture was bubbled through 14 mL of the solution at 25 °C. The O_3/O_2 mixture was generated from an Azcozon RMU 16-04EM ozone generator. The gas flow rate was adjusted to $300\,\mathrm{L\,h^{-1}}$ to give rise to an ozone concentration of about $0.027\,\mathrm{g\,L^{-1}}$ of the gaseous mixture. A typical treatment time of about 5 min was used. This pretreatment time gave rise to a peroxide content of about $1.3 \times 10^{-5}\,\mathrm{mol\,g^{-1}}$ of the polymer. The dependence of peroxide concentration and molecular weight of FPI on the ozone treatment time under similar experimental conditions had been reported earlier [18]. The ozone-pretreated FPI solution (containing about 1 g of FPI) and 1 mL of the DMF solution of PDB ($1.46 \times 10^{-1}\,\mathrm{mol\,L^{-1}}$) were transferred to an ampoule. DMF solution of PEGMA was then introduced into the ampoule to give a final volume of 20 mL and a PEGMA concentration ranging from 0.11 to $0.26\,\mathrm{g\,mL^{-1}}$. The ampoules were degassed with three freeze–evacuate–thaw cycles. They were then sealed and heated at 60 °C for 6 h. After the desired reaction time, the reactor flasks were cooled in an ice bath. Each FPI-*g*-PEGMA copolymer sample was precipitated in an excess amount of ethanol, and recovered by filtration. The copolymer sample was purified thrice by redissolving in DMF and reprecipitating in ethanol. It was further purified by washing in excess ethanol for another 48 h. Since ethanol is a good solvent for the PEGMA homopolymer, the homopolymer of PEGMA generated during the RAFT-mediated graft copolymerization process should have been extracted out completely. Finally, the copolymer samples were dried by pumping under reduced pressure overnight at room temperature.

2.3. Preparation of the MF membranes

Each microfiltration membrane was prepared by phase inversion in an aqueous medium from a 12 wt% DMF solution of the copolymer. The copolymer solution was cast onto a glass plate, which was then immersed in a bath of doubly distilled water (nonsolvent) after the polymer solution had been subjected to a brief period of evaporation in air. The temperature of the water in the casting bath was controlled at 22 °C. Each membrane was left in water for about 20 min after separation from the glass plate. It was then extracted in a second bath of double-distilled water at 70 °C for 15 min. Such a heat treatment step was commonly performed during the fabrication of commercial membranes in order to refine the pore size distribution [19]. The purified membranes were dried by pumping under reduced pressure for subsequent characterization. The processes for the RAFT-mediated synthesis of the FPI-*g*-PEGMA copolymer and the preparation of the MF membrane are illustrated in Scheme 1.

2.4. Characterization

Proton nuclear magnetic resonance (^{1}H NMR) was performed on a Bruker ARX 300 instrument with deuterated DMF as the solvent. Gel permeation chromatography (GPC) was performed using THF as the eluent and polystyrene standards as the references. The thermal properties of the copolymers were measured by thermogravimetric analyses (TGA). The samples were heated to 700 °C at a heating rate of $20\,^{\circ}\mathrm{C\,min^{-1}}$ under a dry nitrogen atmosphere in a Du Pont Thermal Analyst 2100 system, equipped with a TGA 2050 thermogravimetric thermal analyzer. X-ray photoelectron spectroscopy (XPS) measurements were made on a Kratos AXIS HSi spectrometer with a monochomatized Al Kα X-ray source (1486.7 eV photons) at a constant dwelling time of 100 ms and a pass energy of 40 eV. The anode current was 15 mA. The pressure in the analysis chamber was maintained at 5×10^{-8} Torr or lower during each measurement. The membranes were mounted on the standard sample studs by means of double-sided adhesive tapes. The core-level signals were obtained at the photoelectron take off angle (α, with respect to the sample surface) of 90 °. Surface elemental stoichiometries were determined from peak-area ratios, after correcting with the experimentally determined sensitivity factors, and with reliable to ±5%. The surface morphology of the MF membranes was studied by scanning electron microscopy (SEM), using a JEOL 6320 electron microscope. The membranes were mounted on the sample studs