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Grafting in confined spaces: Functionalization of nanochannels of track-etched membranes

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HIGHLIGHTS

- The current developments in grafted track-etched membranes were discussed.
- The reader was directed to the most recent selected literature on this subject.
- The unique benefits of incorporation of grafting by CRP methods have been emphasized.
- Examples are given for biotechnology, energy and environmental applications.

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ABSTRACT

Developments in the field of membrane science and specialty applications have given rise to track-etched membranes with nanochannels having broad ranges of functionality and versatile opportunities. This review is a compilation of the recent progress in methods and applications of grafting inside confined spaces in nanoscale. The emphasis has been made on functionalization of nanochannels of track-etched membranes. Selected current literature on track-etched membranes having nanochannels grafted with various polymers has been reviewed in terms of potential applications of the resulting membrane in the fields of biotechnology, energy and environment.

1. Introduction

The emphasis on synthesis and applications of grafted polymers has increased in the past decade. Graft copolymerization has a bright future as a versatile technique that enables the modification of base polymers by incorporating a variety of new molecular functionalities to their structures. The intelligent combination of base polymers with desired monomers containing appropriate functional groups yields synthetic copolymers or modified natural materials with tailor-made specifications designed for target applications. Grafting of different monomers on base polymers can be carried out via various techniques based on chemical, photochemical, and radiation or plasma-induced methods (Bhattacharya and Misra, 2004). Each method has inherent advantages and the choice of a certain method over others depends on the properties of base polymer and monomer in question and degree of grafting needed.

The science and technology in nanoscale are growing rapidly in scope and impact due to potential applications in various fields such as medicine, environment and energy (Champion et al., 2008; Odom and Pileni, 2008). Methods for the synthesis of polymeric nanomaterials are limited to a few strategies such as heterogeneous polymerization, e.g. emulsion polymerization, dispersion polymerization, etc. and self-assembly of block copolymers in a suitable solvent. On the other hand, fabricating micro-/nanostructures on a solid-state substrate using heavy ion irradiation and track-etching technique opens reliable alternate routes to micro- and nano-technology (Barsbay et al., 2013).

Nanoporous materials that maximize surface area/volume ratio of materials offer confined spaces. Typically, these spaces are large enough to allow diffusion of monomers and thus grafting of polymers provided that active species, e.g. radicals, exist within the pores. At the same time, they are small enough for the efficient isolation of certain amount of polymer chains from one another too. This allows for the production of polymers with characteristics not necessarily the same as the corresponding bulk polymers (Hayward et al., 2001; McCoy and Curro, 2002; Ng et al., 1997; Kageyama et al., 1999). Mesoporous silica is an example providing confined channels suitable for homopolymerization initiated catalytically (Kageyama et al., 1999) or by free-radicals (Ng et al., 1997). Along with homopolymerization, surface grafting inside the nanochannels has also been carried out via ATRP initiators

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attached to the pores of mesoporous silica (Kruk et al., 2005). The following part of this short review is intended to direct the reader to selected current literature where grafting occurs on the walls of confined nanochannels; typically those in track-etched membranes rather than other alternatives of confined environment such as the pores in mesoporous alumina or silica.

2. Grafting in nanopores of track-etched membranes: overview and applications

Track-etched polymer membranes are prepared typically from films of polyethylene terephthalate (PET), polycarbonate (PC), polyimide, and fluorinated polymers like poly(vinylidene fluoride) (PVDF). The process involves irradiation of polymer thin films with accelerated heavy ions creating a damaged zone along the track and controlled chemical etching of the degraded regions to yield the cylindrical pores. The pore size of resulting membranes increases with etching time and pore size distribution may be very sharp (Cuscito et al., 2007; Bessbousse et al. 2011). When a membrane with semi-crystalline nature, such as PVDF, is irradiated by accelerated heavy ions very stable radicals are formed. After certain etching times, some radical population is found to survive at the nanopore walls along the tracks. Both the carbon centered radicals and peroxy radicals resulting from air contact in the etched zones can initiate grafting under appropriate conditions. In the presence of vinyl monomers, grafting may be initiated on the nanopore walls of track etched membranes via these residual radicals (Bessbousse et al. 2011; Barsbay et al., 2013, Espinoza et al., 2014). Additionally, post-irradiation may be carried out for grafting following the diffusion of monomer into the nanochannels (Spohr et al., 1998; Reber et al., 1998, 2001). In a few examples, other strategies such as binding a thermal initiator inside the nanochannels are employed for grafting (Yameen et al., 2009a; Nasir et al., 2012). Typically, conventional free radical polymerization technique is carried out during grafting in nanochannels. In order to synthesize novel membranes with controlled architecture, controlled free-radical polymerization (CRP) methods like ATRP (Alem et al., 2008; Friebe and Ulbricht, 2007; Yang and Ulbricht, 2012) and RAFT (Barsbay et al., 2013) have also been utilized in nanochannel grafting. Incorporation of these CRP methods to nanochannel functionalization seems very promising as these techniques provide the accurate control of the degree of grafting and the graft lengths inside the nanochannels thus not plugging the pores for further applications. Fig. 1 shows a schematic representation of the RAFT mediated control of the graft lengths inside the nanochannels. Regardless of the technique used, i.e. conventional or CRP methods, grafting of nanochanels of track-etched membranes seem to be a promising key technology in developing novel membranes. The current literature of track-etched membranes having nanochannels grafted with various polymers is gathered below in terms of their potential applications.

2.1. Biotechnological application

In nature, the ion channels play a key role in selective flow of ions and small organic molecules across the cell membrane. Inspired from the biological ion channels, researchers attempt to develop biosensing systems based on nanochannels (Ali et al., 2011a, 2009; Buchsbaum et al., 2013; Han et al., 2011; Miles et al., 2013). There are three main kinds of nanochannels, namely biological channels embedded in a lipid bilayer, synthetic solid-state nanochannels, and hybrids of biological and synthetic nanochannels (Haque et al., 2013). The solid-state nanochannels fabricated in track-etched membranes have a great potential in biotechnological applications as biomolecule sensors (Ali et al., 2013, 2011a, 2008; Han et al., 2011; Healy et al., 2007; Harrell et al., 2006), stimuli-responsive devices (Reber et al., 2001;

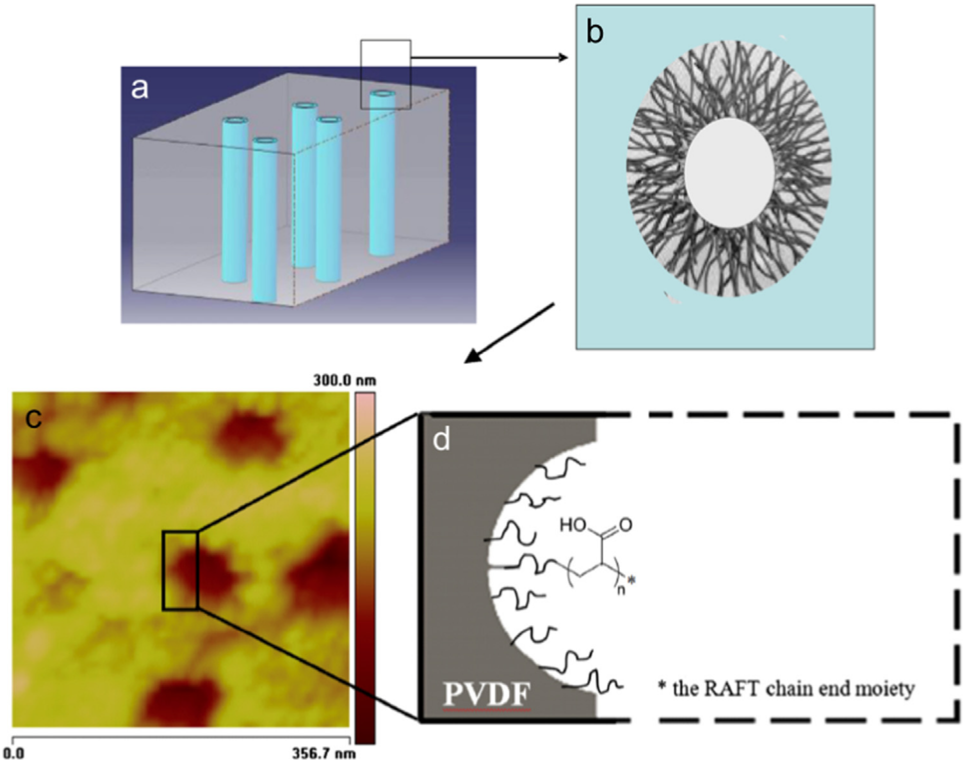

Fig. 1. (a) Scheme of functionalized track-etched nanoporous PVDF membrane; (b) pore interior showing the well-organized grafts on the nanochannel walls by RAFT mediated radical polymerization; (c) AFM image of track-etched PVDF membrane with nanochannels grafted with poly(acrylic acid) (PAA), and (d) chemical description of the pore interior covered by PAA grafted chains ended by the RAFT moiety (Barsbay et al., 2013).