



Multifunctional thiols as additives in UV-cured PEG-diacrylate membranes for CO₂ separation

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ABSTRACT

The utility of incorporating only 20 mol% of multifunctional thiols into UV-cured poly(ethylene glycol) diacrylate (PEGDA) membranes for CO₂ separation is presented. Five different multifunctional thiols were investigated, spanning a range of functionalities from 2 to 4 and also different rigidities. All thiol-modified networks exhibited lower modulus values according to both small-strain and large-strain mechanical testing. This decrease in modulus was primarily attributed to a decrease in crosslink density via the step-growth thiol-acrylate reaction. Decreased crosslink density was more pronounced for dithiol additives which formed a “train-like” topology of connected PEGDA segments. Because of this more linear topology, dithiol-modified networks exhibited increases in gas permeability and strain at break. CO₂ selectivity of each thiol-modified network was nearly comparable to the unmodified PEGDA network. Each network rapidly reached 100% conversion under a nitrogen atmosphere. However in air, the pure acrylate network reached negligible conversion while the networks modified with tri and tetrathiols reached noticeably higher conversions. Outdoor sunlight curing revealed that all thiol-modified networks were tack-free after only several minutes depending on thiol functionality. In contrast, the pure acrylate membrane remained tacky and uncured on the surface indefinitely. This study emphasizes the importance of thiol monomer selection in diminishing oxygen inhibition in UV-initiated acrylate polymerization as well as marked improvement in permeability for this specific PEGDA network via the incorporation of dithiols.

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1. Introduction

Gas separation is an important industrial process with applications such as hydrogen recovery, air separation, and natural gas purification [1]. Often, costly and/or polluting methods like distillation and amine treatment are used. Membrane separation is an environmentally friendly alternative to these methods and polymeric membranes in particular could be manufactured in large quantities and at low cost making them extremely attractive [1–4].

Since the early 1980s, it has been well documented that membranes based on poly(ethylene glycol) (PEG) have a high selectivity for carbon dioxide (CO₂) [5–9], a common contaminant in many industrial gas purification processes as well as a key component in atmospheric packaging for certain foods [10]. It was suggested that the reason for this selectivity is a Lewis acid–base interaction between the polar, electron-rich ether units on the polymer backbone (the Lewis base) and CO₂ (the Lewis acid) [5]. This electronic interaction promotes a high CO₂ solubility in PEG. Solubility

selectivity is an attractive quality since low T_g , rubbery materials may be used. Such materials do not undergo physical aging and can also have extremely high permeability. While it has a low T_g , solid polymeric PEG unfortunately crystallizes to approximately 70 vol% which severely reduces the permeability of the membrane [8,9]. Because gas separation membranes must be highly permeable as well as highly selective [11,12], semi-crystalline PEG would not meet performance requirements for industrial separations.

One solution to the problem of PEG crystallinity is to crosslink PEG, limiting the molecular weight of linear segments between junction points therefore preventing crystallinity [7–9]. The Freeman research group has reported on a multitude of crosslinked amorphous PEG-based membranes made with UV-initiated radical photopolymerization of acrylates based on PEG [13–16]. These membranes show high performance compared to other polymeric CO₂ separation membranes while at the same time employing the inherent advantages of UV-curing such as rapid preparation of large areas of material, no solvents (100% reactive liquid components), energy efficient processing compared to thermal methods, and enormous latitude in formulations due to the variety of commercially-available UV-curable monomers and oligomers [17,18]. UV-curable materials might also be used to repair defects in gas separation membranes or as coatings to upgrade existing units.

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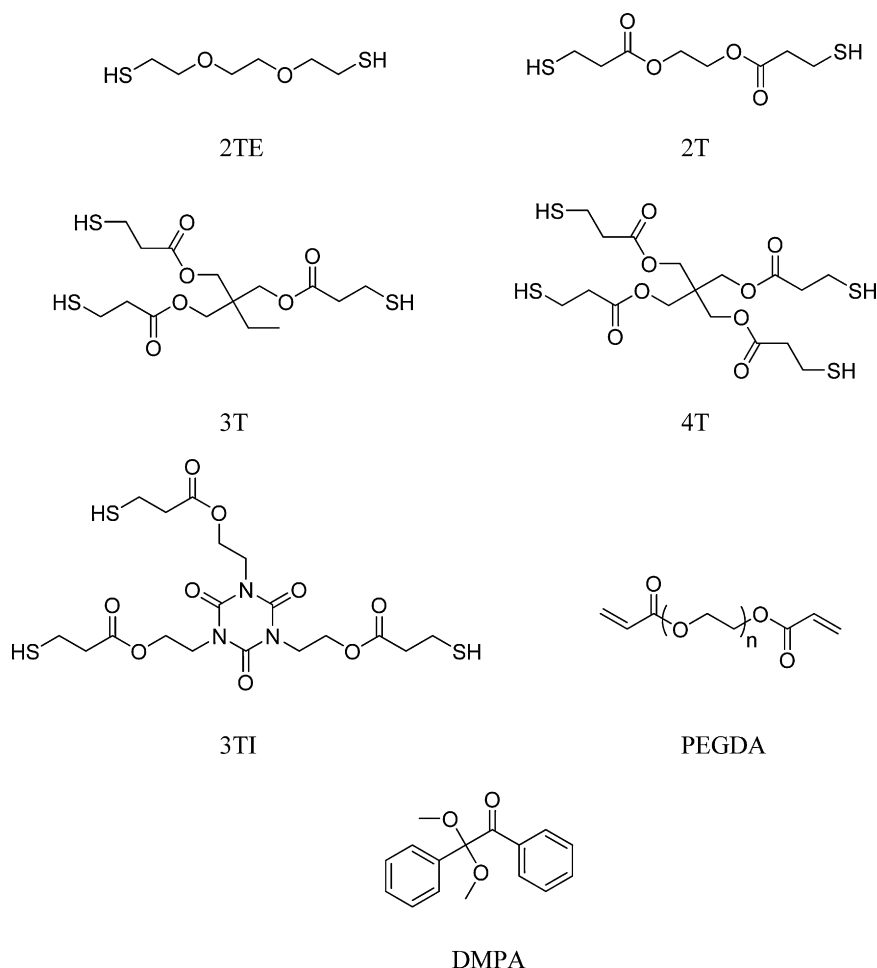


Fig. 1. Structures of thiol monomers, acrylate oligomer, and photoinitiator.

An important drawback to acrylate photopolymerization is oxygen inhibition [17,18]. When cured in an oxygen-containing atmosphere, acrylate radicals react with oxygen forming peroxy radicals. These peroxy radicals are relatively unreactive toward acrylate double bonds thus limiting the overall conversion of these materials when cured in air. As a result, acrylate-based materials are often prepared under a controlled nitrogen atmosphere in order to reach optimal conversions and to prevent an uncured, tacky surface. Thiol–ene photopolymerization, which proceeds via a step-growth free-radical polymerization process compared to the chain-growth acrylate polymerization process, is known for its insensitivity towards oxygen [19–21]. Peroxy radicals formed during polymerization in air readily abstract hydrogen from thiols, generating thiyl radicals which react with double bonds continuing the polymerization process. This thiol–ene photopolymerization process consumes oxygen that diffuses into the liquid mixture and reaches high conversion as in a controlled inert atmosphere. An extensive review of the problems and solutions associated with oxygen inhibition in UV-cured materials is available in reference [22]. In this work, one solution to oxygen inhibition in acrylate photopolymerizations was investigated [22]. By incorporating multifunctional thiols into the acrylate formulation, the effect of oxygen inhibition was diminished. It was hypothesized that polymer system viscosity was a controlling factor for the extent of oxygen inhibition: higher viscosity reduced oxygen diffusion into the system thus decreasing oxygen inhibition [22].

We previously studied oxygen transport and free volume in a variety of basic and modified thiol–ene networks all UV-cured

in air [23,24]. It is our intent to expand the range of applicability of UV-cured thiol–enes into membrane applications while employing the advantages of the well-defined and robust thiol–ene reaction. In this paper, we demonstrate the benefits of incorporating only a small amount of various multifunctional thiols into a PEG-based acrylate membrane, poly(ethyleneglycol)diacrylate. Multifunctional thiol monomers will be ranked based on how they affect gas separation performance as well as their efficacy towards correcting the oxygen inhibition problem during UV-initiated processing.

2. Experimental

2.1. Materials

The thiol monomers glycol di(3-mercaptopropionate) (2T), trimethylolpropane tri(3-mercaptopropionate) (3T), and pentaerythritol tetra(3-mercaptopropionate) (4T) were supplied by Bruno Bock Thio-Chemical-S. Thiol monomer ethylenedioxy diethanethiol (2TE) was obtained from Aldrich. Thiol monomer tris[2-(3-mercaptopropionyloxy)ethyl] isocyanurate (3TI) was obtained from Wako Pure Chemical Industries. Acrylate oligomer poly(ethylene glycol)diacrylate (PEGDA) with average $M_n = 700$ g/mol was obtained from Aldrich. All mixtures were initiated using the photoinitiator 2,2-dimethoxy-2-phenylacetophenone (DMPA) which was also obtained from Aldrich. All materials, shown in Fig. 1, were used as received.

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