

UV-Cured Membranes for Gas Separation

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Gas separation (GS) membranes are an eco-friendly, cost-effective method to separate gaseous mixtures.¹ Such membranes can be produced and operated inexpensively in order to replace costly and, in some cases, polluting commercial gas-separation techniques such as distillations or amine treatments. Natural gas purification, hydrogen recovery, air separation, atmospheric scrubbing and dehydration are some of the more common applications for GS membranes.¹ In 1991,² and later updated in 2008,³ Robeson reported an upper-bound limit between the permeability of polymer membranes and their

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permselectivity for different gases. He demonstrated that a trade-off exists between the two properties. For high selectivity one must sacrifice flux (productivity) and vice versa.^{2,3} Naturally, there is an industrial interest in developing membranes that beat the upper bound limit, (i.e., a membrane with high permeability and high selectivity).

GS membranes operate on the principle of selective permeation or

permselectivity. According to the solution-diffusion equation ($P = D \cdot S$), there are two components which may be tuned to increase permselectivity—diffusivity selectivity (D_A/D_B) and solubility selectivity (S_A/S_B) (1):⁴

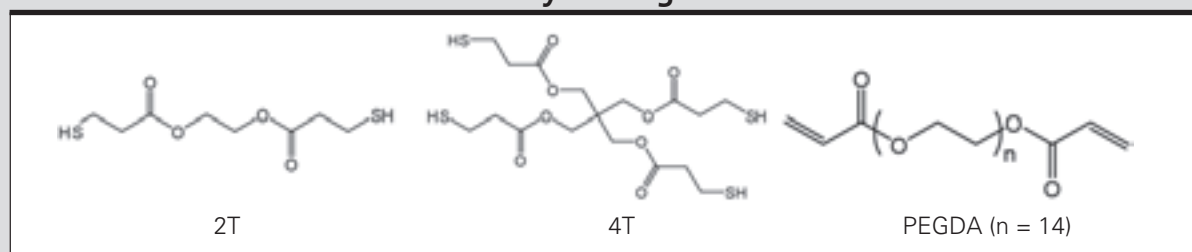
$$\frac{P_A}{P_B} = \left(\frac{D_A}{D_B} \right) \left(\frac{S_A}{S_B} \right) \quad (1)$$

Zeolite molecular sieves are known for their uniform and fixed-pore sizes that separate small molecules based on diffusivity (or size) selectivity. Because zeolite membranes are expensive and relatively fragile, high- T_g glassy polymers with rigid backbones (such as polyimides and polysulfones) have been explored and are used commercially as diffusivity selective membranes.⁴

Solubility selectivity is another route by which gas mixtures containing polar gases such as CO_2 and H_2S can be separated. One advantage of solubility-selective membranes is that rubbery, low T_g polymers (which do not undergo physical aging) can be used since the permselectivity is based on chemical affinity rather than gas molecule size. In particular, poly(ethylene glycol) (PEG)-based polymer membranes have a very high solubility-selectivity for CO_2 transport.⁶ The polar ethylene glycol repeat units have a strong affinity for CO_2 molecules which have quadrupolar moments.⁶ This affinity dramatically increases the permeability of CO_2 through the membrane compared to other gases such as N_2 , O_2 , CH_4 and even H_2 , which is a reverse-selective process due to H_2 being smaller in

FIGURE 1

Structures of thiol monomers and acrylate oligomer



size than CO_2 .⁶ Membranes based on PEG have been shown to approach or even beat the “upper bound” in certain CO_2 separation processes⁶⁻⁷ and have also been regarded as a potentially promising material approach with applications in methane and hydrogen purification as well as atmospheric scrubbing for life support systems or power plant flue gas.⁶

GS membranes are processed typically by extrusion or solution casting followed by spiral winding or hollow-fiber spinning.⁴ Less commonly, UV curing has been used to fabricate GS membranes.⁶⁻⁸ UV-photopolymerization is a rapid, efficient and well-established method of curing liquid monomers and oligomers into solid polymer films.^{9,10} The advantages of UV curing are widely known—rapid processing of large areas of material; tunable properties since a wide variety of acrylated oligomers and thiol-enes are available; eco-friendly due to 100% reactive components (no solvents) and high energy efficiency; and the flexibility of coating to a variety of substrates or as free-standing films.^{9,10} UV-curable membranes might also be used to repair defects in existing GS membranes or as coatings which enhance their performance.

In this work, the permeation of oxygen and carbon dioxide in UV-cured, thiol-modified networks were evaluated. Advantages of incorporating only a small

amount of multifunctional thiols into a PEG-based acrylate are presented.

Experimental

Materials

The thiol monomers glycol di(3-mercaptopropionate) (2T) pentaerythritol tetra(3-mercaptopropionate) (4T) were supplied by Bruno Bock Thio-Chemical-S. 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 1-hydroxycyclohexyl-phenyl ketone (HCPK or Irgacure 184) supplied by Ciba Specialty Chemicals.

All materials were used as received.

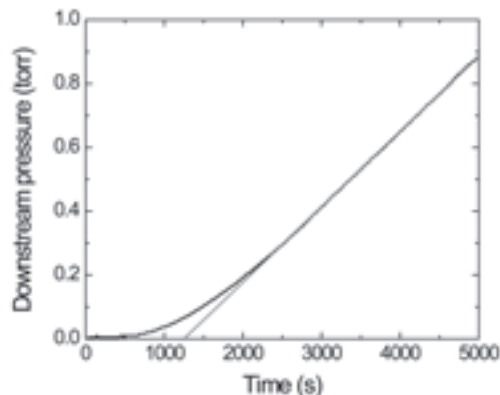
Preparation of films

For the control material, PEGDA, 1 wt% HCPK was added to the PEGDA and then sonicated for 10 minutes. This mixture was then poured onto a glass plate and sandwiched by another glass plate with a shim to control the thickness. This glass plate/oligomer sandwich was then cured using 10 passes at 10 ft/min feed speed under a Fusion UV-curing line system with a D bulb (400W/cm² with belt speed of 10 feet/min and 3.1 W/cm² irradiance). For thiol-acrylate mixtures, 20 mol% (based on total functional groups) of

FIGURE 2

Actual Fickian flux curve for N_2 permeation through a 550 micron PEGDA+4T membrane

Black curve is actual experimental data for permeated gas pressure while gray line is an extrapolation of the steady-state slope.



thiol was added to PEGDA. HCPK was then incorporated at 1 wt%, sonicated and cured as already described. This procedure was used both with 2T as the thiol additive and 4T as the thiol additive.

Characterization

Permeation of oxygen and carbon dioxide were measured using a custom-built gas permeation device based on a constant-volume, variable-pressure (manometric) technique. Upstream feed gas pressure was monitored with an Omega Engineering pressure transducer. Downstream-permeated gas pressure was monitored with an MKS 226A differential pressure transducer. Both transducers were connected to a computer for real-time data collection. Permeation cells were maintained at a constant 23°C via a recirculating chiller. All film samples were degassed using high vacuum for 24 hours prior to testing.

Functional group conversions for all networks were monitored using a Bruker 88 FTIR spectrometer modified with a fiber-optic cable to irradiate samples sandwiched between two salt plates. The conversion of acrylate double bonds at 810 cm^{-1} was

TABLE 1

Permeabilities of CO_2 and O_2 and the resulting pure-gas selectivity measured at 23°C for each membrane

	P_{CO_2} (Barrer)	P_{O_2} (Barrer)	Selectivity ($\text{P}_{\text{CO}_2}/\text{P}_{\text{O}_2}$)
PEGDA	53	2.2	24
PEGDA+2T	66	2.7	24
PEGDA+4T	49	2.3	21

monitored as a function of irradiation time. An Oriel 200 W high-pressure, mercury-xenon lamp with light intensity of 6.16 mW/cm^2 at 365 nm was used to irradiate the samples and invoke photopolymerization. Both air and nitrogen-curing atmospheres were investigated.

Tack-free time studies for films cured in sunlight were conducted on the roof of the USM School of Polymers and High Performance Materials building. Films were drawn down at 4 mil thickness onto steel substrates. Total solar radiation was 90 mW/cm^2 and the UV index was 10 as recorded by a Davis Advantage Pro 2 weather station.

Results and Discussion

A typical experimental permeation curve using the technique described in the Experimental section is shown in Figure 2. This example specifically is a 550-micron PEGDA+4T membrane tested for N_2 permeability. The black curve is experimental data reported by the differential pressure transducer. The gray line is an extrapolation of the steady-state slope portion and is used to calculate P .

From these curves, permeability values for O_2 and CO_2 for each membrane were generated and are listed in Table 1. The thiol-modified membranes exhibited selectivity values comparable to the unmodified PEGDA control. A slight increase in permeability for both gases was observed for the membrane modified with 2T is a difunctional monomer and likely reduced the crosslink density of the network. Overall, it is clear from Table 1 that the addition of only a small amount of multifunctional thiols to a PEGDA mixture maintains the gas separation performance of the original PEGDA membrane.

Acrylate group conversions were studied as a function of UV-irradiation time as described in the experimental section. As expected, under a nitrogen atmosphere all three networks rapidly reached 100% conversion of acrylate groups as shown in Figure 3. Actual spectra from the first (pre-curing) IR

FIGURE 3

Fractional conversion of acrylate functional groups for three networks under nitrogen atmosphere

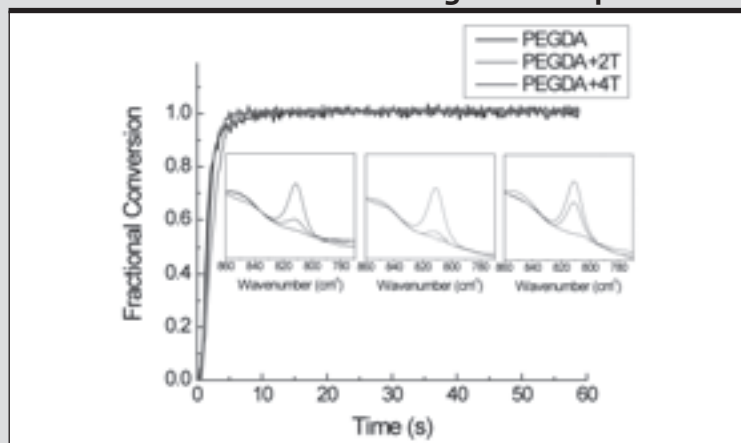
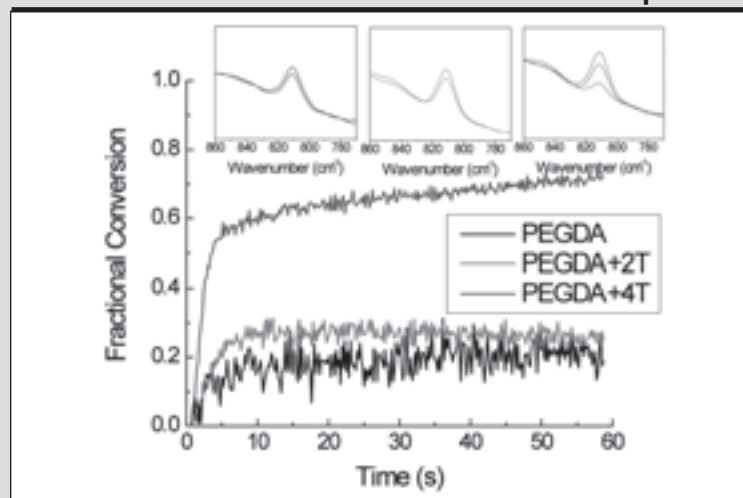


FIGURE 4

Fractional conversion of acrylate functional groups for three networks under ambient air atmosphere



scan, a mid-conversion scan and a fully cured scan are provided as insets.

Note that in these networks, the acrylate double bonds homopolymerize while the thiols add into the acrylate double bonds; these reactions happen simultaneously. No measurable differences in rate or total conversion were expected or observed. However, without a nitrogen blanket (i.e., in ambient air) the fractional conversions of each network show striking differences as seen in Figure 4.

Both the PEGDA control network and the PEGDA+2T thiol-modified network reach low acrylate conversions even after 60 seconds. In contrast, the PEGDA+4T thiol-

modified network attains 50% conversion after only 5 seconds and nearly 70% conversion after 60 seconds. This result demonstrates the utility of incorporating a multifunctional thiol into a PEG-based diacrylate oligomer when curing in an air atmosphere. The free-radical, step-growth thiol-ene reaction is uninhibited by oxygen because peroxy radicals readily abstract hydrogen from thiols, regenerating thiyl radicals and continuing the polymerization process.¹¹ The free-radical, chain-growth acrylate homopolymerization reaction is, however, hindered by oxygen due to the relative unreactivity of peroxy radicals toward acrylate double bonds.^{10,12}

To further highlight the energy efficiency and eco-friendly advantages of the thiol-ene reaction, tack-free time studies were performed on 4 mil films of each network using sunlight in outdoor ambient air. As seen in Table 2, sunlight is able to cure the thiol-modified networks as compared to the PEGDA control which was still tacky on the surface after nearly 4 hours. This is in contrast to the PEGDA+4T membrane which left no tack after only 5.5 minutes.

The tack-free time studies, along with the curing atmosphere investigations using RT-FTIR, demonstrate that these specific acrylate-based, UV-curable membranes may be fabricated in air and at faster line speeds (less UV light intensity) with the addition of 20 mol% multifunctional thiols. Furthermore, using renewable sunlight to fabricate 100% reactive component mixtures into GS membranes would make for a truly environmentally conscious approach to replace existing energy-intensive gas separation techniques.

Conclusions

UV-photopolymerized thiol-acrylate membranes were fabricated and tested for CO₂/O₂ separation performance. While indicating comparable gas separation performance, the incorporation of multifunctional thiols into PEG-based acrylated oligomers allowed for air atmosphere curing and also sunlight curing outdoors, demonstrating the environmental friendliness and energy efficiency of this approach. Present work is aimed at developing and testing new thiol-based, UV-curable networks for high-performance CO₂ gas separation. Correlations between crosslinking density, ethylene glycol content, feed gas pressure, and membrane performance and durability were discussed in the presentation.

TABLE 2

Tack-free times for each membrane when cured with sunlight under ambient outdoor air conditions

Material	Tack-free Time (sec)
PEGDA+4T	330
PEGDA+2T	900
PEGDA	14,000+

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