Functionalization of Poly(oxindole biphenylene) Membranes by Photoinduced Thiol-Yne Click Chemistry

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Abstract

The modification of poly(oxindole biphenylene) (POXI) membranes by photoinduced thiol-yne click strategy is described. First, a propargyl-functionalized porous poly(oxindole biphenylene) (POXI-PG) membrane was prepared by condensation reaction of isatin and aromatic hydrocarbons with a superacid-catalysis. Subsequently, the solution and surface functionalization of POXI-PG by one-step photoinitiated thiol-yne click reaction with various thiol functional molecules, namely pentaerythritol tetrakis(3-mercaptopropionate) (PETMP), 1,2-ethanedithiol (EDT) and thiol functional poly(ethylene glycol) methyl ether (PEG-SH) was demonstrated. The successful modification of POXI was confirmed by the spectral and thermal investigations via ¹H NMR, FT-IR, XPS and DSC analyses. The POXI-PG membranes crosslinked with PETMP had the molecular weight cut off (MWCO) reduced from 75 to 5 kg mol⁻¹. They became stable in different organic solvents with permeations between 0.4 to 3.8 L m⁻² h⁻¹ bar⁻¹.

Keywords: Poly(oxindole biphenylene), membrane, photoinduced thiol-yne click reaction, surface modification

1. Introduction

The implementation of the membrane technology for a growing diversity of applications with demanding requirements, such as stability in organic solvents and controlled wetting properties, can highly benefit from simple and efficient chemical modification methods. The use of photochemical reactions in synthetic polymer chemistry has attracted considerable attention and has provided unconventional and efficient routes to synthesize complex macromolecular structures. There are number of photochemical approaches for the synthesis and functionalization of complex macromolecular structures, including conventional and controlled/living photopolymerizations, and photoiniduced click reactions¹⁻⁷. A large number of types of strategies have been thoroughly explored and developed during last several decades⁸⁻¹². However, the main problem of these processes is the requirement of metal catalyst that mostly hinder their use in biological applications. Strain-promoted azide–alkyne cycloaddition, thiol-yne and thiol-ene coupling, thiol-ene Michael addition and Diels-Alder cycloaddition are the well-established metal free click reactions that offer several advantages including fast reaction kinetics, extensive functional group tolerance and mild reaction conditions¹³⁻¹⁹. Among them, thiol-yne click reactions have an additional feature that one alkyne group can react with two thiol groups to form multifunction materials and highly cross-linked polymers with high sulfur content²⁰⁻²⁴. Thiol-yne reactions can be triggered either by base, transition-metals and thermally or photochemically generated free-radicals²⁵. The proposed mechanism for photochemically generated free radical mode is illustrated in Figure 1.

Figure 1. Photo induced radical mediated mechanism of the thiol-yne click reaction

Accordingly, thiyl radicals formed by photochemical hydrogen abstraction reactions essentially yield thioether type adducts with a high degree of anti-Markovnikov selectivity within two reaction cycles.

The present study introduces a photo induced thiol-yne click strategy to attach functional group or polymers to the surface of polyoxindolebiphenylene (POXI) membranes or promote their crosslinking. POXI has been recently explored for membrane application due to its high thermal and chemical stability. (B. A. Pulido et al. J. Membr. Sci. 2017, 539, 187) (J. Membr. Sci. 2018, 564, 361) The benefits of this strategy are the relatively easy protocol, metal-free feature, tolerance to a variety of functional groups and spatial and temporal control. As will be shown below, the click component side-chain alkyne functional POXI can successfully be modified with mono thiol functional poly(ethylene glycol) (PEG-SH) and various low molar mass compounds with different thiol functionalities. Further on, the structural and thermal characterization of the prepared membranes before and after modification were investigated by ^1H NMR, FT-IR, XPS and DSC analyses.

2. Materials and methods

2.1. Materials

Biphenyl (Aldrich, 99.5%), isatin (Aldrich, 97%), potassium carbonate (K_2CO_3 , Aldrich, 99%), trifluoromethanesulfonic acid (Aldrich, 98%) trifluoroacetic acid (Alfa Aesar, 99.5%), *N*-methyl-2-pyrrolidone (Aldrich, 99%), propargyl bromide (Aldrich, 80% toluene solution), phenylacetylene (Aldrich, 98%), propargyl alcohol (Aldrich, 99%), pentaerythritol tetrakis(3-mercaptopropionate) (Aldrich, >95%), 1,2-ethanedithiol (Aldrich, >98%), 2,2- dimethoxy-2-phenylacetophenone (DMPA) (Acros Organics, >95%), 3-mercaptopropionic acid (Aldrich, >99%), poly(ethylene glycol) methyl ether (Me-PEG) (M_n :2000 g mol $^{-1}$, Aldrich), magnesium sulfate anhydrous ($\geq 99.5\%$, Aldrich), sodium bicarbonate ($\geq 99.5\%$, Aldrich), sulfuric acid (Aldrich, 95-98%), toluene ($\geq 99.5\%$, Aldrich), dichloromethane ($\geq 99.8\%$, Aldrich) were used as received without any further purification. All solvents were used as received.

2.2. Polymer chemical and thermal characterization

^1H -NMR measurements were recorded with $\text{Si}(\text{CH}_3)_4$ as internal standard, using an Agilent NMR System VNMRS 500 spectrometer. FT-IR spectra were recorded on a Perkin-Elmer FT-IR Spectrum One-B spectrometer. Differential scanning calorimetry was performed on a PerkinElmer Diamond DSC from 30 to 320 $^\circ\text{C}$ with a heating rate of 10 $^\circ\text{C min}^{-1}$ under nitrogen

flow (20 mL min⁻¹). Contact angle measurements were carried out by using a contact angle system (DataPhysics Instruments, Germany).

2.3. Synthesis of POXI

The POXI synthesis followed a previously reported methodology (B. A. Pulido et al. J. Membr. Sci. 2017, 539, 187). Biphenyl (1.542 g, 10 mmol), trifluoroacetic acid (4.65 mL) and trifluoromethanesulfonic acid (8.00 mL) were magnetically stirred in a 25 mL single-neck round-bottom flask. The mixture was cooled down with an ice-water bath. The isatin (1.4715 g, 10 mmol) was added swiftly to the mixture. The reaction was kept under N₂ atmosphere. The ice-water bath was removed 10 minutes after the reaction started. The reaction was allowed to continue at room temperature for 3 h. The resulting high viscous reaction solution is quenched by pouring it into methanol. The obtained white fiber is then filtered and copiously washed with methanol and dried in vacuum-oven overnight.

2.4. Synthesis of POXI-PG

The alkyne functionalization of POXI was performed, by adapting a procedure previously reported by B. Pulido et al. (J. Membr. Sci. 2018, 564, 361), as in Scheme 1. POXI (1 g) and *N*-methyl-2-pyrrolidone (19 mL) were magnetically stirred in a 50 mL single-necked round-bottom flask. Once a transparent homogeneous solution was obtained, potassium carbonate (2 g, 14.4 mmol) was added. Propargyl bromide (80% toluene solution) (2 mL, 18.5 mmol) was added to the reaction mixture dropwise. The reaction was kept at room temperature and N₂ atmosphere during 24 h. The reaction was quenched in water. The obtained yellow fibers are washed with water and methanol and then dried in vacuum-oven overnight.

Scheme 1. Synthesis of POXI-PG.

2.5. Synthesis of PEG-SH

In a 250 mL flask equipped with a stirrer, Me-PEG (10 g, 5 mmol) was mixed with mercaptopropionic acid (1.6 g, 15 mmol) in 100 mL toluene. Then, 3 drops of H₂SO₄ (98%) was added and refluxed at 120 °C in a Dean-Stark apparatus. After all water was collected in the trap, the mixture was cooled, and the solvent was evaporated in vacuo. The residue was dissolved in CH₂Cl₂ (100 mL) and washed with NaHCO₃ for three times. After drying with MgSO₄, it was filtered, concentrated and precipitated into cold diethyl ether. The white solid was dried at room temperature under vacuum overnight.

2.6 General procedure for photoinduced thiol-yne click reaction in solution

A general experimental procedure for the photo-induced thiol-yne click reaction was as follows: POXI-PG (1 eq.) solutions with 1,2-ethanedithiol (2 eq.), pentaerythritol tetrakis(3-mercaptopropionate) (2 eq.) or PEG-SH (101 mg, 0.8 eq.), and DMPA (0.02 eq. for monomers and 0.8 eq. for polymer) in 0.5 ml of THF were combined in a Schlenk tube equipped with a magnetic stirrer. The solution was purged with N₂ for 5 min. The reaction tube was irradiated by using a Rayonet merry-go-round photoreactor, in which the sample was surrounded by a circle of 16 lamps emitting light nominally at 350 nm. After 2 h, the products obtained with each monomer were washed with excess of methanol and acetone. The product of the reaction with PEG-SH was diluted and precipitated in 10-fold excess of diethyl ether. The solid was dried at room temperature under vacuum overnight.

2.7 General procedure for photoinduced thiol-yne click reaction on surface

A general experimental procedure for the photo-induced thiol-yne click reaction on the membrane surface was as follows: solutions of 1,2-ethanedithiol, pentaerythritol tetrakis(3-mercaptopropionate) (2 eq.) or PEG-SH (4 eq.), and DMPA (0.04 eq.) in 2 ml of acetone were combined in a Schlenk tube equipped with a magnetic stirrer in the presence of POXI-PG preformed membranes (~1 eq.). The reaction tube was irradiated by using in a Rayonet merry-go-round photoreactor in which the sample was surrounded by a circle of 16 lamps emitting light nominally at 350 nm. After 2 h, the modified membranes were washed with excess acetone a few times and then dried in vacuum-oven overnight at r.t.

2.8 Contact Angle Measurements. The surface hydrophilicity of functionalized membranes was investigated by contact angle measurements. Water contact angles (WCA) on surfaces of dry membranes were measured by using a contact angle system (DataPhysics Instruments, Germany) at ambient temperature. The membrane surfaces were 0.5–1 cm² wide. A water

droplet of 3 μl was deposited on the surface of each dry membrane and contact angles were measured. All reported values are the average of four measurements taken at different locations of an individual membrane.

2.9 Membrane performance. The membranes permeances to water, dimethyl formamide (DMF), dimethyl sulfoxide (DMSO), N-methyl pyrrolidone (NMP) and tetrahydrofuran (THF) were measured in dead-end filtration cells under stirring at 5 bar and room temperature. A membrane area of $??\text{ cm}^2$ was used for the measurement. The molecular weight cut-off (MWCO) is defined as the minimum molecular weight 90 % rejected by the membranes. The value was obtained by analysing by gel chromatography (GPC) the composition of the feed, permeate and retentate in filtration experiments of ?? wt% (total concentration) solutions containing a mixture of different molecular weights of poly(ethylene glycol) (PEG) in water and DMF.

Results and Discussion

In the present work, we establish a photo-induced thiol-yne click reaction as an easy and robust methodology for the modification of POXI, used as membrane in organic solvent operations at high temperatures. The first critical issue concerns the appropriate functionalization of click components. The alkyne functional POXI was prepared according to a condensation reaction of isatin and aromatic hydrocarbons in the presence of a super acid catalysis, followed by functionalization with propargyl bromide (Scheme 1). The ^1H NMR spectrum (Figure S1) verifies the successful synthesis of POXI and POXI-PG. The original amide proton of the unmodified POXI (signal at $\delta = 10.85\text{ ppm}$) is replaced by the propargyl signals at $\delta = 4.61\text{ ppm}$ and $\delta = 2.27\text{ ppm}$ in the ^1H NMR spectrum.

By using the alkyne substituted polymer POXI-PG as a starting material we proposed here a platform for further functionalization based on thiol-yne click reactions, which can easily provide membranes with different properties, tailored for different applications. We focused in this work mainly on poly(ethylene glycol) (PEG) grafting and two crosslinking reactions, as summarized in Scheme 2.

Scheme 2. Photoinduced thiol-yne click reactions explored in this work.

The potential advantages for grafting PEG to membranes are the following. First, when applied for filtrations in aqueous medium, the PEG grafting could promote the formation of more hydrophilic membranes and increase their fouling resistance, which is an important issue in the water sector (*Industrial & Engineering Chemistry Research* 56 (23), 6785-6795). On the other hand, if the material will be considered for the preparation of membranes for gas separation, PEG segments are known to preferentially favour the transport of CO₂ over other gases, as reported before for other PEG-based membranes (*Macromolecules*, 2010, 431, 326-333).

The PEG-macromolecular click component, PEG-SH, was synthesized by Fischer esterification of hydroxyl functional poly(ethylene glycol) methyl ether (Me-PEG, M_n :2000 g mol⁻¹) with mercaptopropionic acid in good yield (Scheme 3).

Scheme 3. Synthesis of PEG-SH.

The structural and thermal characterization of PEG-SH was investigated by spectral and thermal analysis. The ¹H-NMR spectra presented in Figure 1 showed that the COOH peak of mercaptopropionic acid at 12.24 ppm completely disappeared while the new peaks developed after the esterification reaction at 3.32-3.80 ppm corresponding to the PEG segment. The successful esterification was also evidenced by FT-IR spectra analysis. As can be seen from Figure 3, the carbonyl band appearing at 1698 cm⁻¹ shifted to 1736 cm⁻¹ after the esterification

process. The disappearance of the broad vibration band between 2200-3400 cm^{-1} arising from the intra- and intermolecular hydrogen bonding is an additional evidence for the successful functionalization of PEG.

Figure 2. ^1H NMR spectra of mercaptopropionic acid and PEG-SH in $\text{DMSO}-d_6$ and CDCl_3 , respectively.

Figure 3. FT-IR spectra of mercaptopropionic acid (a), Me-PEG (b) and PEG-SH (c).

In order to gain more insight into the process, first the photo-induced thiol-yne click reaction between POXI-PG and PEG-SH was conducted in solution. Upon the irradiation of a THF solution containing both click components in the presence of 2, 2- dimethoxy-2- phenylacetophenone (DMPA) at 350 nm, the corresponding graft copolymer (POXI-g-PEG) is readily formed (Scheme 4).

Scheme 4. Synthesis of POXI-g-PEG by photoinduced thiol-yne click chemistry.

The ^1H NMR spectra of the precursors display characteristic protons of acetylene and PEG functionalities. After the click reaction, the proton signals of $-\text{CH}_2-\text{N}$ at 4.59 ppm shifted to 4.28 ppm and the acetylenic proton ($-\text{CH}$) peak at 2.24 ppm disappeared, while the new peaks corresponding to PEG segments at 3.28-3.94 ppm appeared. Notably, aromatic protons of POXI before and after grafting resonate at around 7.00 -7.65 ppm. These results indicate that the click reaction was attained with quantitative yield.

Figure 4. ^1H NMR spectra of POXI-PG and POXI-g-PEG in CDCl_3 .

The successful grafting was also confirmed by FT-IR analysis (Figure 5). Apparently, the peak at 3293 cm^{-1} attributed to the acetylenic side moiety completely disappeared after the photolysis. The peaks at 1600 cm^{-1} and 700 cm^{-1} are specific to POXI units.

Figure 5. FT-IR spectra of (a) POXI-PG, (b) PEG-SH and (c) POXI-g-PEG.

The thermal behaviour of the precursors and graft polymer thus formed was investigated by DSC. As can be seen from Figure 6, the characteristic melting temperature (T_m) of the PEG unit for the graft copolymer appears between $40\text{--}52\text{ }^\circ\text{C}$ while the melting point of the PEG precursor before the reaction was detected at $55\text{ }^\circ\text{C}$. Similar shifts were previously observed for graft copolymers possessing PEG side chains²⁶.

Figure 6. DSC traces of (a) POXI-PG, (b) Me-PEG and (c) POXI-g-PEG.

Besides the functionalization with PEG, the photo-induced thiol-yne click reaction strategy was used in this work for polymeric membrane crosslinking. Crosslinking is particularly important to improve the chemical resistance of membranes aiming at applications in the chemical industry for separations to be conducted in an organic solvent medium. Since POXI-PG possesses alkyne side groups in the structure, it is anticipated that cross-linked networks can readily be formed through the described photoinduced click reaction with multi thiol functional molecules in solution or in preformed membranes immersed and/or swollen with the appropriate reactive chemicals. Upon irradiation of POXI-PG and related thiol components in THF at 350 nm in the presence of DMPA as photoinitiator, a complete gelation occurred after 2h (Figure 7).

Figure 7. Photographs of a clickable POXI solution, which contains POXI-PG, PETMP and DMPA in THF (a) before and (b) after thiol-yne click reaction, under irradiation at 350 nm.

The network structure was analysed by FTIR (Figure 8). As can be seen, after the incorporation of PETMP structure, the ester carbonyl appeared at 1733 cm^{-1} . The broad band around 1150 cm^{-1} corresponds to the -C-O- vibrations of the thiol component.

Figure 8. FT-IR spectra of (a) POXI-PG and (b) its network structure with PETMP.

In the light of the information gained from the photoinduced grafting in solution, the corresponding two-phase reactions were conducted to modify the properties of the preformed POXI membranes. In these experiments, the same thiol compounds used for the reactions in solution were employed for the surface modifications. Similar photoirradiations of the mixtures of POXI-PG with acetone solutions of thiols and DMPA resulted in the incorporation of the thiol moieties on the surface of the membrane by interfacial thiol-yne click reaction (Scheme 5). Notably, while reactions with PEG-SH resulted in the formation of hydrophilic surfaces, cross-linked structures are formed with multifunctional thiols.

Scheme 5. Schematic representation of the thiol-yne photo-click reaction for the surface modification of POXI-PG membranes.

XPS was used to monitor the changes in the surface chemical composition of POXI-PG membranes after the thiol-yne click reaction. As can be seen from Figure 9, where binding energies of initial POXI-PG membrane and its modified surfaces are presented, the peaks of C-H, C-C, C-N, C-O and C=O have appeared around 285 eV in the core level spectrum of C 1s. In the XPS spectra of the modified surfaces, two new peaks at 160 and 225 eV have appeared corresponding to S 2p of S, C-S and S-H. Expectedly, nitrogen N 1s and oxygen O 1s peaks were observed for all the specimens at 400 eV and 540 eV, respectively. These results indicated that the thiol components have been successfully incorporated onto the membrane surface and some of thiol functionalities remained unreacted due to the limited reactions of the all thiol groups on the solid surface. However, this would provide a possibility for further functionalization. (The exact values of eV peaks can be rewritten from the original data).

Figure 9. XPS wide scan spectra of (a) POXI-PG, (b) POXI-PEG, (c) EDT and (d) PETMP modified membranes.

In order to evaluate the wettability of the modified surfaces, the water contact angles on the membrane surfaces were measured (Figure 10). The obtained values were 90.1° , 75.5° , 64.7° and 54.0° for POXI-PG, EDT, PETMP and PEG-SH modified surfaces, respectively. The modification with PEG-SH led to the formation of more hydrophilic surface, because of its characteristic polyether structure. The values obtained for the surfaces modified with multifunctional thiol compounds are similar to those previously reported in the literature for other thiol-based modifications²⁷. Notably, PETMP modified surfaces exhibited relatively higher hydrophilicity due to the higher number of thiol functions.

Figure 10. Water contact angle measurements of (a) POXI-PG, (b) EDT, (c) PETMP and (d) PEG-SH modified membrane surfaces.

Membrane performance

The water permeance of POXI-PG, dithiol and tetra-thiol modified membranes were evaluated. The permeance of the unmodified membrane POXI-PG is $117 \text{ L m}^2 \text{ h}^{-1} \text{ bar}^{-1}$, as shown in Figure 11. The rejection test was done by filtering a solution of different molecular weights PEG through the membrane. According to the GPC elugram for the PEG solutions and the rejection curve showed in Figure 12, the molecular weight cut off (MWCO) of the POXI-PG membrane is close to $75,000 \text{ g/mol}$.

Figure 11. Water permeance of the POXI-PG membrane.

Figure 12. (a) GPC-elugram and (b) rejection curve for POXI-PG membranes in water.

The membranes crosslinked with the dithiol and tetra-thiol (PETMP) were stable in organic solvents, confirmed in experiments performed with pressure of 5 bar. All membranes were mechanically robust in organic solvents, such as DMF, DMSO, NMP and THF. The membranes functionalized with dithiol and PEG-SH had a very low water permeance, indicating that the functionalization was highly efficient, but an optimization under milder conditions would be necessary to tailor the membrane performance for liquid separation.

The permeance and rejection of membranes modified with PETMP are display in Figure 13 and 14. The water permeance is $3.8 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ with a rejection around 5 kg mol^{-1} . The permeances of the same membrane in different organic solvents are shown in Figure 15 (left) and the relationship among permeance and solvent viscosity in Figure 15a. The permeance values decrease with the increase of the viscosity. Except for THF, all solvents follow a linear function, indicating that the membranes are stable in these solvents and no swelling or pore size change affect the permeance.

Figure 13. Water permeance of POXI-PG after modification with PETMP.

Figure 15. (a) GPC-elugram and (b) rejection curve in DMF for POXI-PG modified with PETMP.

Figure 15. (a) Permeance of various solvents and (b) permeance as a function of solvent viscosity for the POXI-PG membrane modified with PETMP.

Conclusion

A novel methodology for the solution and surface modifications of POXI and membranes prepared therefrom by photoinduced thiol-yne click reaction is proposed. Alkyne-functionalized POXI membrane were further modified with low molar mass di- (EDT) and tetratiols (PETMP) and a polymeric (PEG) thiol via one-step UV-initiated thiol-yne click reaction. The success of the process was confirmed by spectral and thermal analyses. As demonstrated by water contact angle measurements, the hydrophilicity of the membranes can be tuned by the type of the thiol compound and extent of the click reaction. The permeability and molecular weight cut off (MWCO)s of the pristine and modified membranes were investigated. We demonstrated here the modification with 3 modifying molecules, but it is clear that the described approach can be extended to any membranes possessing alkyne groups allowing incorporation of different desired functional groups on to the surface or crosslinkers in a simple manner with high efficiency. The objective of this paper is to demonstrate the method. Although not presented here in detail, the possibility of spatial and temporal control of the process under milder or intenser reaction conditions makes the approach particularly attractive for the design and application of new membrane materials.

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