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Post Modification of Acetylene Functional Poly(oxindole biphenylene) by Photoinduced CuAAC

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Abstract

A novel strategy to obtain side chain modified poly(oxindole biphenylene) (POXI) by photoinduced copper(I)-catalyzed azide-alkyne cycloaddition (CuAAC) click reaction is described. In the first step, an alkyne-functionalized poly(oxindolebiphenylene) (POXI-alkyne) is synthesized by superacid-catalyzed condensation of isatin with aromatic hydrocarbons. Subsequently, poly(ethylene glycol) methyl ether (Me-PEG), 1-pyrenemethanol (Py-OH) and 1,3-dibromopropane (DBP) are functionalized by azide groups via simple nucleophilic substitution reaction. Visible-light-induced CuAAC reaction between POXI-alkyne and the corresponding azide functionalized click components employing dibenzoyldiethylgermane (DBDEG) as photoactivator resulted in the formation of POXI-PEG, POXI-Py and insoluble network, respectively. Successful modification of POXI was confirmed by the spectral, (¹H NMR, FT-IR, Fluorescence), chromatographic (GPC) and thermal (DSC) investigations.

Keywords: Photo-induced CuAAC, grafting, poly(oxindolebiphenylene), poly(ethylene glycol), pyrene

1. Introduction

Polymeric membranes are now being used in many separation processes[1], such as gas purification, vapour recovery, water desalination and purification and hemodialysis. There are still many opportunities in the chemical industry[2], which have not been explored yet. The growth of membrane application in chemical industry strongly depends on the availability of polymeric materials with exceptional physical properties, thermal and chemical stability[3]. The hydrophilicity or the interaction with permeating solvent is important. Functionalization can improve targeted specific separations. On the other hand, the use of membranes in organic solvents requires different forms of crosslinking to avoid membrane damage by partial solubilisation. The development of better membranes for chemical and pharmaceutical industry is a growing field. Cross-linked polyimide, polybenzimidazole and polyetherketone are some of the high-performance materials being used for membranes with solvent stability[4-7]. We have been focusing on polytriazoles[8, 9] poly(oxindolebiphenylene)[10] (POXI), polymers with exceptional thermal stability, which extend the window of application of polymeric membranes to conditions currently only covered by ceramic analogues.

One way to combine distinct properties of structurally different polymers in membranes is to form graft copolymers which can be accomplished by “grafting from” and the “grafting to” approaches[11]. In the “grafting from” approach, polymerization process is carried out by starting directly from the side-chain initiator functional surfaces. However, the second approach involves covalent bonding of the prefabricated polymer chains to the surface. The “grafting to” approach has some disadvantages for conventional coupling reactions. Steric hindrance and reactivity limitations during the reaction, prevents to obtain homogeneous and dense polymer membranes. The copper-catalyzed azide-alkyne cycloaddition (CuAAC) reaction allows precise control over the desired structure synthesis. Simplicity of the “click” reaction permits straight and controllable functionalization or crosslinking in one-step process. In general, click chemistry is one of the most studied classes of organic reactions with numerous superior advantages over the conventional routes including rapidity, versatility, high efficiency and selectivity.

CuAAC click reactions can be triggered by photochemical means and successfully used for the preparation of complex and functional macromolecular structures and, networks [12-22]. It was also shown that such photochemical processes can be combined with the various polymerization routes to prepare block and graft copolymers[18, 23-27] and networks[28-30] in a sequential and *in situ* manner.

As part of our continuous interest in developing novel photochemical routes for macromolecular synthesis, we herein report a flexible “grafting to” approach to impart additional properties to the membrane material POXI by photo induced CuAAC. In the process, first side-chain alkyne functional POXI was prepared as one of the click component and poly(ethylene glycol) methyl ether (PEG-Me), pyrene methanol (Py-OH) and 1,3-dibromopropane were azidated to form reaction partner molecules for the click reaction. The latter molecules were deliberately selected so as to provide representative examples for polymer and functional group grafting and cross-linking, respectively. The intermediates at various stages and ultimate click products were characterized by spectral, chromatographic and thermal investigations.

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%), *p*-toluenesulfonyl chloride (Aldrich, 99%), 1-pyrenemethanol (Aldrich, 98%), sodium hydride (60 % dispersion in mineral oil, Aldrich), propargyl bromide (purum, 80% in toluene), sodium azide (NaN_3 , Panreac, 99%), 1,3-dibromopropane (Aldrich, 97%), poly(ethylene glycol) methyl ether (Me-PEG) (M_n :2000 $g\cdot mol^{-1}$, Aldrich), dibenzoyldiethylgermane (DBDEG) (kindly provided by Ivoclar Vivadent, Liechtenstein), and copper (II) chloride ($CuBr_2$, Acros Organics, 99%), copper (II) bromide (Merck) were used as received without any further purification. Isatin was recrystallized from hot ethanol. Trifluoroacetic acid and trifluoromethanesulfonic acid were distilled prior used. *N,N,N',N'',N'''*-pentamethyldiethylenetriamine (PMDETA, Aldrich, 99%) was purified by passing through basic alumina (Al_2O_3) prior to use. All solvents were used as received.

2.2. Characterization

1H -NMR measurements were recorded with $Si(CH_3)_4$ 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. UV–visible spectra were measured with a Shimadzu UV-1601 double-beam spectrometer. Fluorescence measurements were carried out using a Hitachi F-4500 fluorescence spectrophotometer at room temperature. Molecular weights were

determined by gel permeation chromatography (GPC) instrument, Agilent instrument (1100 series) consisting of a pump and refractive index detector with two Waters Styragel column (HR 3 and HR 2), (7.8 mm internal diameter, 300 mm length) and 1 mL/min DMF flow rate at 35 °C. RI detector was calibrated with polystyrene standards having narrow molecular weight distribution.

2.3. Synthesis of POXI

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. Yield 96%. ¹H-NMR (CDCl₃, 500 MHz): δ (ppm) = 10.80 (s, 1H), 7.60 (d, 4H), 7.25 (m, 6H), 7.02 (b, 2H). IR: 3300 cm⁻¹ (-N-H stretching), 3055 cm⁻¹ (aromatic C-H stretching), 1590 cm⁻¹ (sim. ring stretching), 1505 cm⁻¹ (ring stretching), 780 cm⁻¹ (sim. out-of-plane bending), 680 cm⁻¹ (out-of-plane ring bending).

2.4. Synthesis of POXI-alkyne

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. Yield ~95%. ¹H-NMR (CDCl₃, 500 MHz): δ (ppm) = 7.50 (d, 4H), 7.20 (m, 6H), 7.15 (p, 2H), 4.65 (s, 1H), 2.24 (s, 1H). IR: 3280 cm⁻¹ (-CH₃ stretching), 3060 cm⁻¹ (aromatic C-H stretching), 1600 cm⁻¹ (sim. ring stretching), 1510 cm⁻¹ (ring stretching), 775 cm⁻¹ (sim. out-of-plane bending), 685 cm⁻¹ (out-of-plane ring bending). Raman: 2100 cm⁻¹ (characteristic peak for the alkyne group).

2.5. Synthesis of tosyl-functional poly(ethylene glycol) (PEG-Ts)

Me-PEG (4 g, 2 mmol) and 4-toluenesulfonyl chloride (3.81 g, 20 mmol) with a magnetic stirring bar were added to a 250 mL three-necked round-bottom flask and solved with 100 mL DCM under N₂ atmosphere. Triethylamine (20.2 g, 20 mmol) in CH₂Cl₂ (40 mL) was added dropwise at 0 °C into the mixture and stirring was continued for 24 h at room temperature. The mixture was filtrated and precipitated into cold diethyl ether. The monotosylated poly(ethylene glycol) (PEG-Ts) was obtained as white powder after dried in a vacuum at 25 °C. Yield 75%. ¹H-NMR (CDCl₃, 500 MHz): δ (ppm) = 7.79 (d, 2H), 7.34 (d, 2H), 4.15 (t, 2H), 3.82 (t, 2H), 3.48-3.78 (m, 176H), 3.38 (s, 3H), 2.44 (s, 3H). IR: 3050 cm⁻¹ (aromatic C-H stretching), 1605 cm⁻¹ (sim. ring stretching), 1500 cm⁻¹ (ring stretching), 770 cm⁻¹ (sim. out-of-plane bending), 680 cm⁻¹ (out-of-plane ring bending).

2.6. Synthesis of azide-functional poly(ethylene glycol) (PEG-N₃)

The tosylated PEG (2 g, 1 mmol) was placed into a 250 mL erlenmeyer flask and NaN₃ (1.3 g, 20 mmol) in dry DMF (35 mL) was added under a N₂ atmosphere. The mixture was stirred at room temperature for 24 h. The resulting product was dissolved in CH₂Cl₂, extracted with 5% NaCl several times and then, washed with distilled water for three times to neutralize the solution. Afterwards, solvent was evaporated under vacuum and then precipitated in cold diethyl ether. The solid material was collected by filtration. Finally, the product was dried in vacuum for overnight. Yield 80%. ¹H-NMR (CDCl₃, 500 MHz): δ (ppm) = 3.48-3.78 (m, 176H), 3.38 (t, 2H), 3.37 (s, 3H). IR: 2960 cm⁻¹ (-CH₃ ant. sim. stretching), 2880 cm⁻¹ (-CH₃ sim. stretching), 2860 cm⁻¹ (-CH₂ sim. stretching), 2100 cm⁻¹ (-N₃), 1465 cm⁻¹ (-CH₃ ant. sim. bending), 1455 cm⁻¹ (-CH₂ scissoring bending), 1090 cm⁻¹ (C-O stretching, ant. sim. coupled C-C).

2.7. Synthesis of tosyl-functional pyrene (Py-Ts)

1-Pyrenemethanol (0.75 g, 3.2 mmol) with a magnetic stirring bar in 50 mL single-necked round-bottom flask was dissolved in 10 mL chloroform under a nitrogen atmosphere and cooled in an ice bath (0 °C). Pyridine (1.2 mL, 14.6 mmol) was added to the solution. 4-Toluenesulfonyl chloride (0.9 g, 4.8 mmol) was dissolved in 10 mL of CHCl₃ and slowly added to the cold reaction flask. The reaction mixture was stirred 24 h at room temperature. The solution was extracted with 0.5 N HCl and 5% NaHCO₃. The organic layers were combined and washed with water and dried over Na₂SO₄. After filtration, product was dried in vacuum for overnight. ¹H-NMR (CDCl₃, 500 MHz): δ (ppm) = 7.57-8.40 (m, 9H), 7.30-7.45 (m, 4H), 5.35 (s, 2H), 2.45 (s, 3H). IR: 3040 cm⁻¹ (aromatic C-H stretching), 1600 cm⁻¹

(sim. ring stretching), 1493 cm^{-1} (ring stretching), 1445 cm^{-1} (side ways ring stretching), 775 cm^{-1} (sim. out-of-plane bending), 660 cm^{-1} (out-of-plane ring bending).

2.8. Synthesis of azide-functional pyrene[31] (Py-N₃)

Py-Ts (0.6 g, 1.55 mmol) was placed into a 100 mL single-necked round-bottom flask and NaN₃ (0.3 g, 4.66 mmol) in dry DMF (30 mL) was added under a N₂ atmosphere. The mixture was stirred at 65 °C for 3 days. The resulting product was dissolved in CHCl₃ and extracted with water for various times. Then, to neutralize the solution, washed with distilled water for three times. The organic layer was dried with anhydrous Na₂SO₄ and solvent was evaporated with a rotary evaporator and then precipitated in MeOH. The product was collected by filtration and dried in vacuum for overnight. Yield 60%. ¹H-NMR (CDCl₃, 500 MHz): δ (ppm) = 7.51-8.46 (m, 9H), 5.38 (s, 2H). IR: 3040 cm^{-1} (aromatic C-H stretching), 2100 cm^{-1} (-N₃), 1600 cm^{-1} (sim. ring stretching).

2.9. Synthesis of 1,3-diazidopropane (DAP)

In a flask equipped with a stirrer, 1,3-dibromopropane (1 eq.), sodium azide (5 eq.) and 15 mL DMF were added. The reaction mixture was stirred for 24 h at room temperature and precipitated in 10-fold excess of water to yield of 1,3-diazidopropane. The solid was collected after filtration and dried at room temperature under vacuum overnight. ¹H-NMR (CDCl₃, 500 MHz): δ (ppm) = 3.40 (t, 4H), 1.80 (br, 2H). IR: 2926 cm^{-1} (-CH₂ ant. sim. stretching), 2850 cm^{-1} (-CH₂ sim. stretching), 2100 cm^{-1} (-N₃), 1455 cm^{-1} (-CH₂ scissoring bending).

2.10. PEG functionalization of POXI-alkyne by photo-induced CuAAC (POXI-g-PEG)

To a Schlenk tube equipped with a magnetic stirrer, PEG-N₃ (101 mg, 0.8 eq.), POXI-alkyne (30 mg, 1 eq.), CuBr₂ (6.72 mg, 0.8 eq.), PMDETA (8.2 μL , 0.8 eq.) and DBDEG (17 mg, 0.8 eq.) were added and dissolved in 5 mL DMSO. The reaction mixture was degassed by three freeze - pump - thaw cycles for 2 times. The reaction tube was irradiated by using a Ker-Vis blue photoreactor equipped with a circle of 6 lamps (Philips TL-D 18 W) emitting 400–500 nm light. After 18 h, the mixture was concentrated by a vacuum distillation process and precipitated in 10-fold excess of diethyl ether. The solid was collected after decantation and dried at room temperature under vacuum overnight.

2.11. Pyrene functionalization of POXI-alkyne by photo-induced CuAAC (POXI-g-Py)

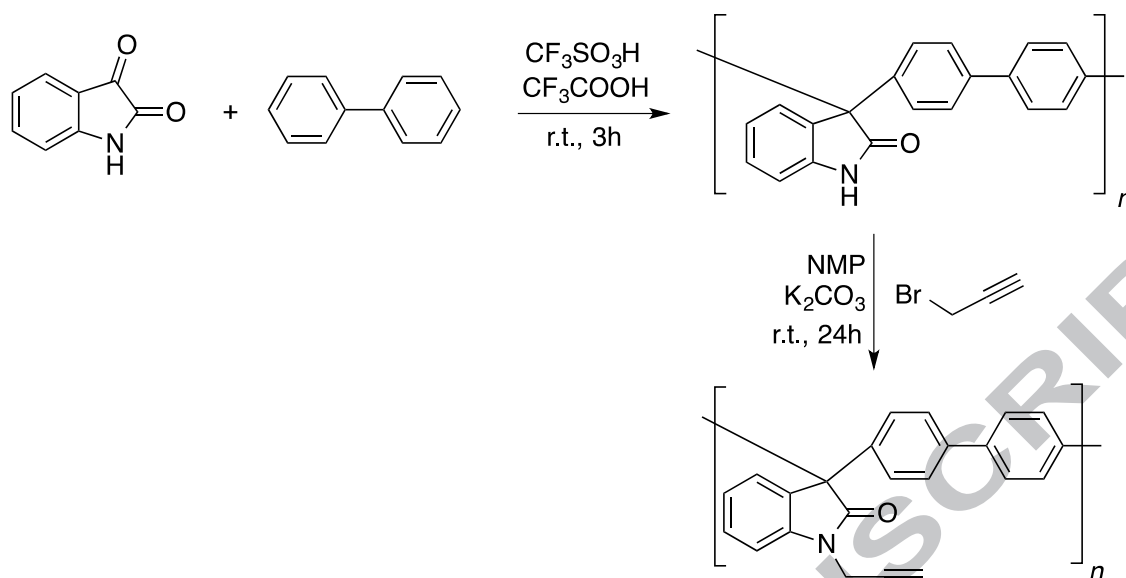
To a Schlenk tube equipped with a magnetic stirrer, Py-N₃ (9.6 mg, 0.8 eq.), alkyne functional membrane (15 mg, 1 eq.), CuBr₂ (8.4 mg, 0.8 eq.), PMDETA (6.2 μ L, 0.8 eq.) and DBDEG (12.8 mg, 0.8 eq.) were added and dissolved in 2.5 mL DMF. The reaction mixture was degassed by three freeze - pump - thaw cycles for 2 times. The reaction tube was irradiated by using a Ker-Vis blue photoreactor equipped with a circle of 6 lamps (Philips TL-D 18 W) emitting light nominally at 400–500 nm. After 18 h, the mixture precipitated in 10-fold excess of methanol to yield POXI-g-Py. The solid was collected after decantation and dried at room temperature under vacuum overnight.

2.12. Crosslinking of POXI-alkyne with DAP by photo-induced CuAAC

DAP (50 μ l, 1 eq.), POXI-alkyne (0.03 g), CuCl₂ (2 eq.), PMDETA (2 eq.) and DBDEG (1.5 eq.) were added to a Schlenk tube equipped with a magnetic stirrer, and dissolved in 10 mL DMSO. The reaction tube was irradiated by using a Ker-Vis blue photoreactor equipped with a circle of 6 lamps (Philips TL-D 18 W) emitting 400–500 nm light. After 24 h, solid like mixture was washed with DMSO and precipitated in 10-fold excess of water. The solid was collected after filtration and dried at room temperature under vacuum overnight.

3. Results and Discussion

In the scope of this study, our main goal was to introduce photo-induced CuAAC click reaction for the modification of POXI, a polymer which is being proposed by our group for the development of membranes for operation in organic solvent medium with high temperature resistance[10]. Different strategies of functionalization and crosslinking were explored. Several approaches for the fabrication of functional polymer membranes have been proposed[32]. These include; i) synthesis of well-defined novel polymer structures as 'tailored' membranes[33, 34], ii) advanced surface functionalization to provide unique barrier constructions[35], iii) the use of templates for creating tailored barriers[36], iv) preparation of mixed matrix or composite membranes[37] and v) novel improved processing of polymers such as thin-layer technologies or miniaturization[38]. For the cross-linking method, usually esterification reactions[39] by using appropriate crosslinkers or one-step phase inversion processes[40, 41] were applied. In our work, photo-induced CuAAC was conducted in solution by using various click components, namely a macromolecular chain, a fluorescent molecule and a cross-linking agent. The solution methodology was deliberately chosen as to get better insight into the mechanism supported by spectral characterization which may further be conveyed to the membrane systems. For this purpose, first clickable POXI was prepared by superacid-catalyzed polycondensation as described previously. This synthetic approach includes a one-pot, metal-free, room-temperature reaction, and allows the preparation of high performance polymers in a short amount of time[42]. The incorporation of the propargyl group to the POXI polymer is achieved by a nucleophilic substitution reaction. The $^1\text{H-NMR}$ spectra show that the N-H (10.60 ppm) peak disappeared while two new peaks corresponding to the $-\text{CH}_2$ (4.65 ppm) and $-\text{CH}$ (2.24 ppm) aroused. The obtained POXI-alkyne is soluble in common organic solvents and could be used for membrane preparation by solution casting.



Scheme 1. Synthesis of POXI-alkyne.

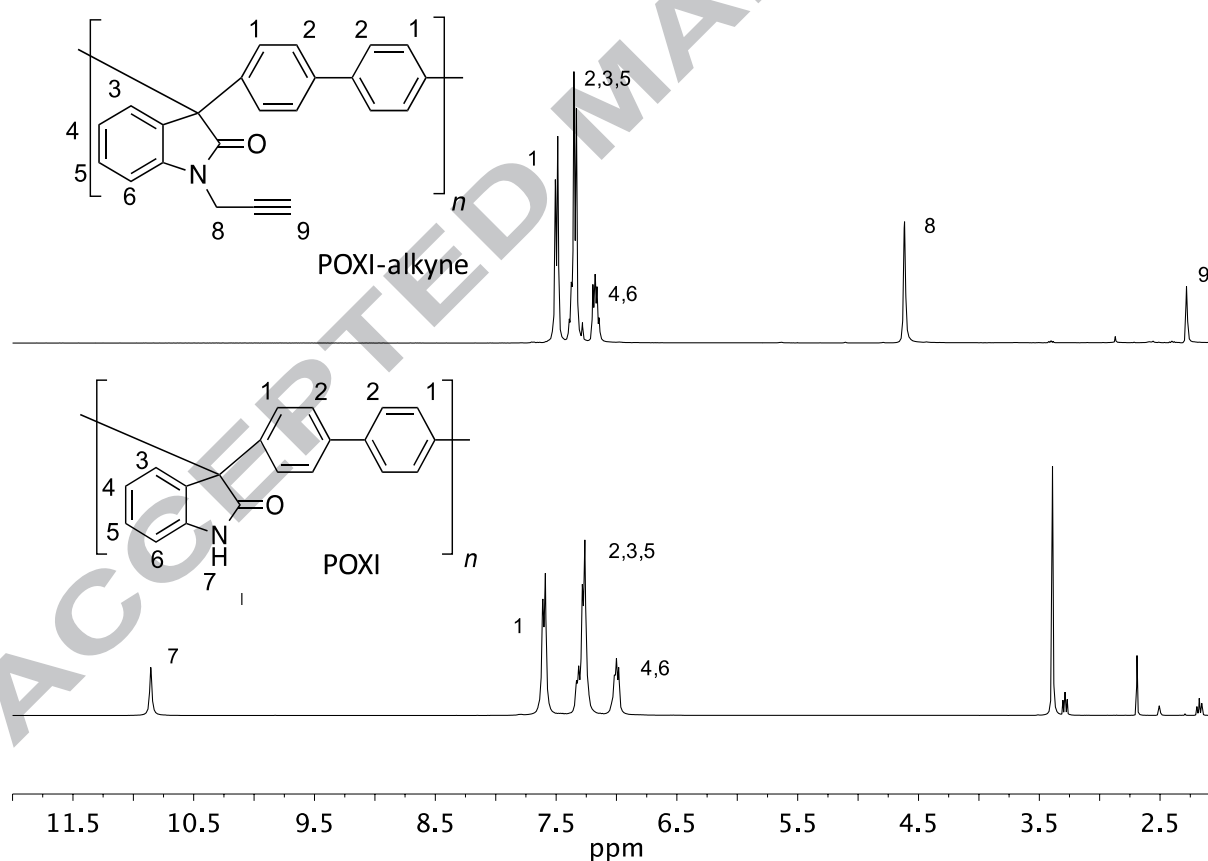
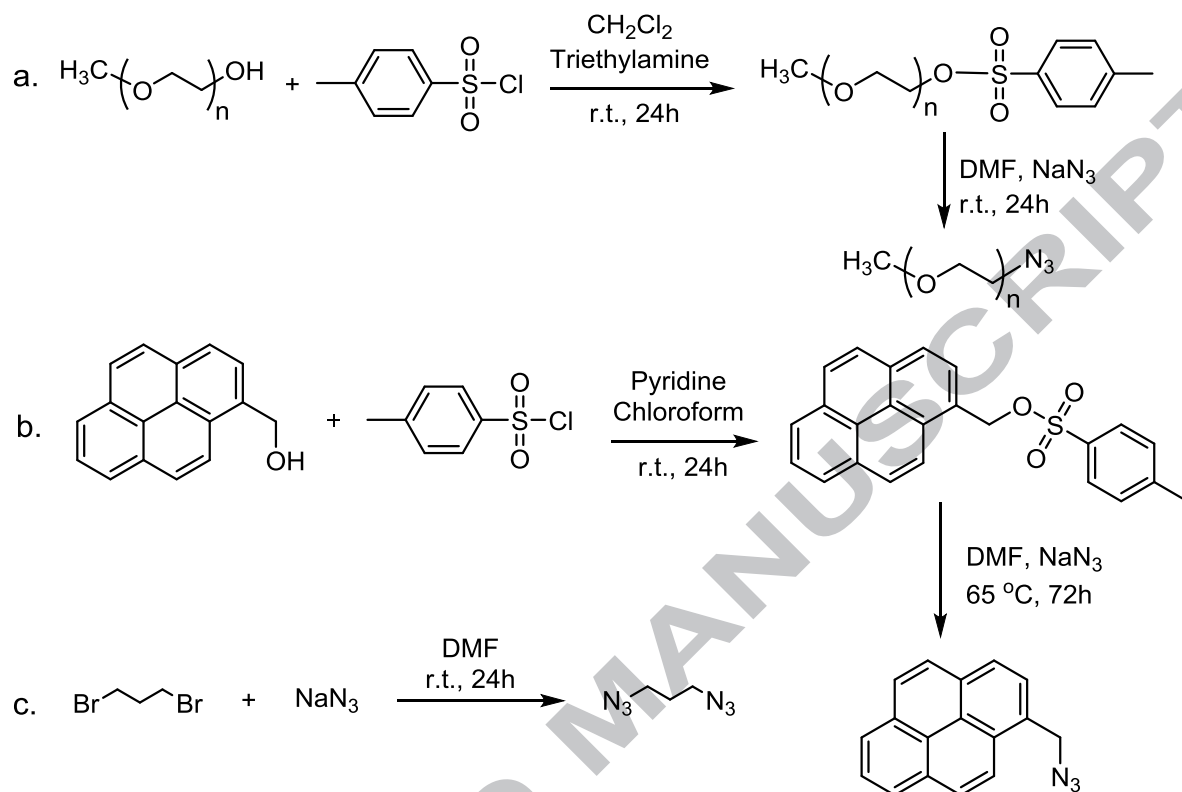


Figure 1. $^1\text{H NMR}$ spectra of POXI and POXI-alkyne.

The reaction partner click components were prepared under standard azidation conditions by tosylation and subsequent azidation process to afford PEG and Py with terminal azide

functionality (PEG-N₃ and Py-N₃, respectively) according to the reaction described in Scheme 2.



Scheme 2. Synthesis of azide functional poly(ethylene glycol) (PEG-N₃) (a), pyrene (Py-N₃) (b) and dibromopropane (DAP) (c).

The chemical structures of the azide functional polymer (PEG-N₃) and low-molar mass azido compounds (Py-N₃ and DAP) were confirmed by spectral analysis. As can be seen from the FT-IR spectra (Figures 2, 3 and S2) the characteristic band of N₃ group emerged around 2100 cm⁻¹.

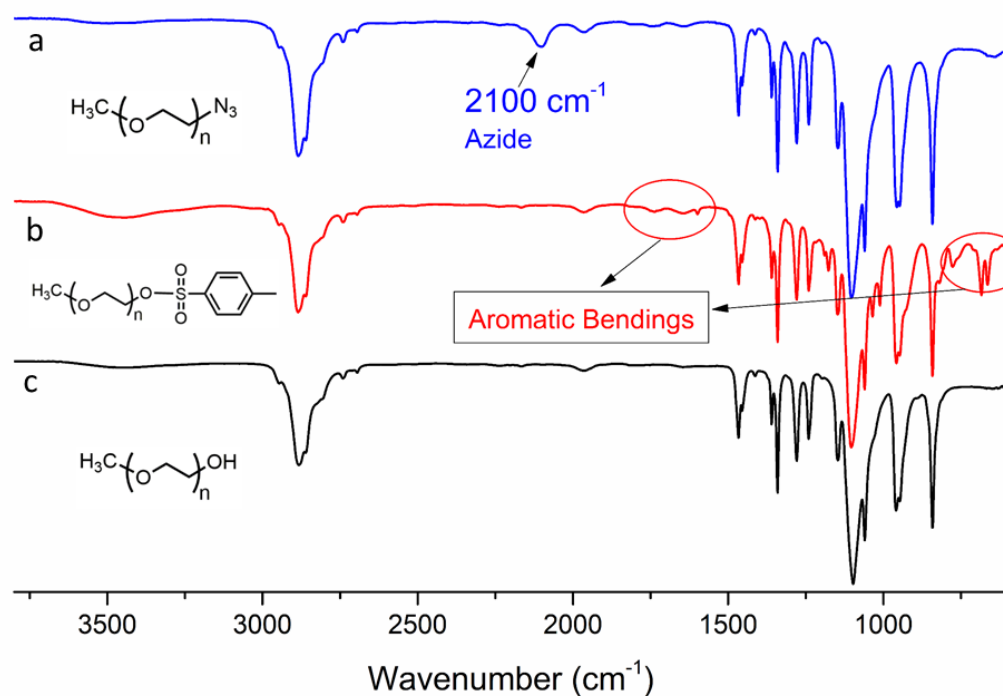


Figure 2. FT-IR spectra of Me-PEG (c), PEG-Ts (b) and PEG- N_3 (a).

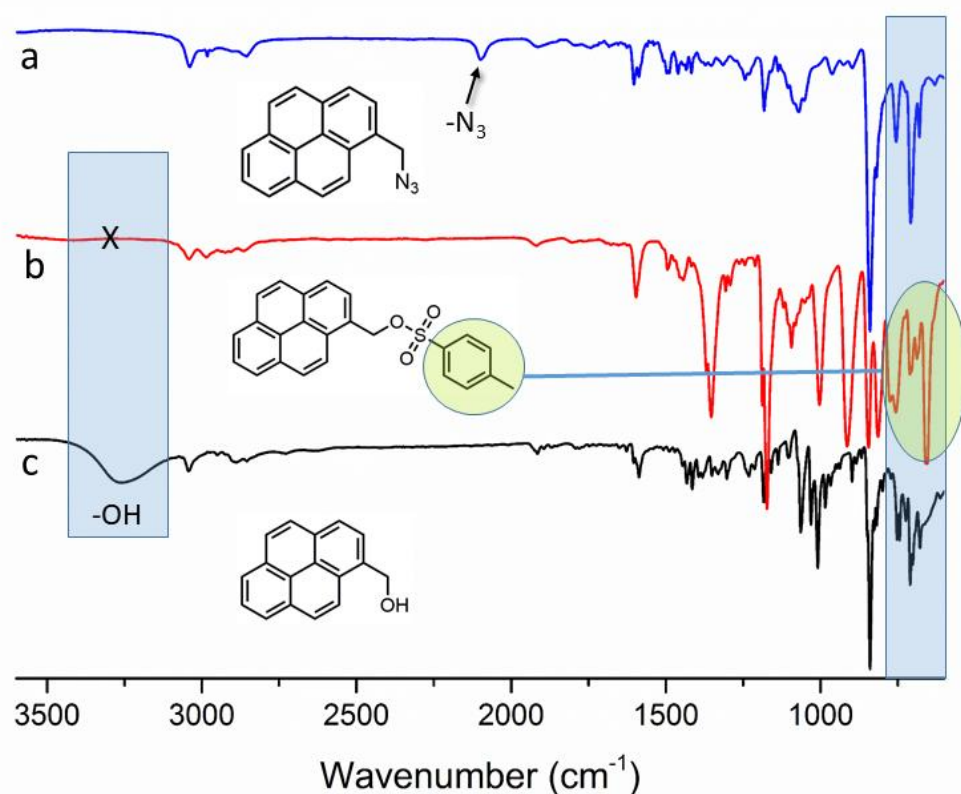


Figure 3. FT-IR spectra of Py-OH (c), Py-Ts (b) and Py- N_3 (a).

As shown in Figure 4, the ^1H NMR spectrum of the Py-OH showed signal at 5.42 ppm which is assigned to CH_2 protons adjacent to the pyrene ring. Aromatic protons of the pyrene units

appeared around 7.9–8.4 ppm. After tosylation reaction, new aromatic protons and $-\text{CH}_3$ protons of tosyl groups emerged at 7.38 ppm and 2.47 ppm, respectively. Aromatic protons and $-\text{CH}_3$ protons of tosyl groups completely disappeared after the azidation process indicating a quantitative reaction. The ^1H NMR spectrum of the DAP showed a slight shift around 3.40 and 2.00 ppm which is assigned to CH_2 protons adjacent to halogen group (Figure S1).

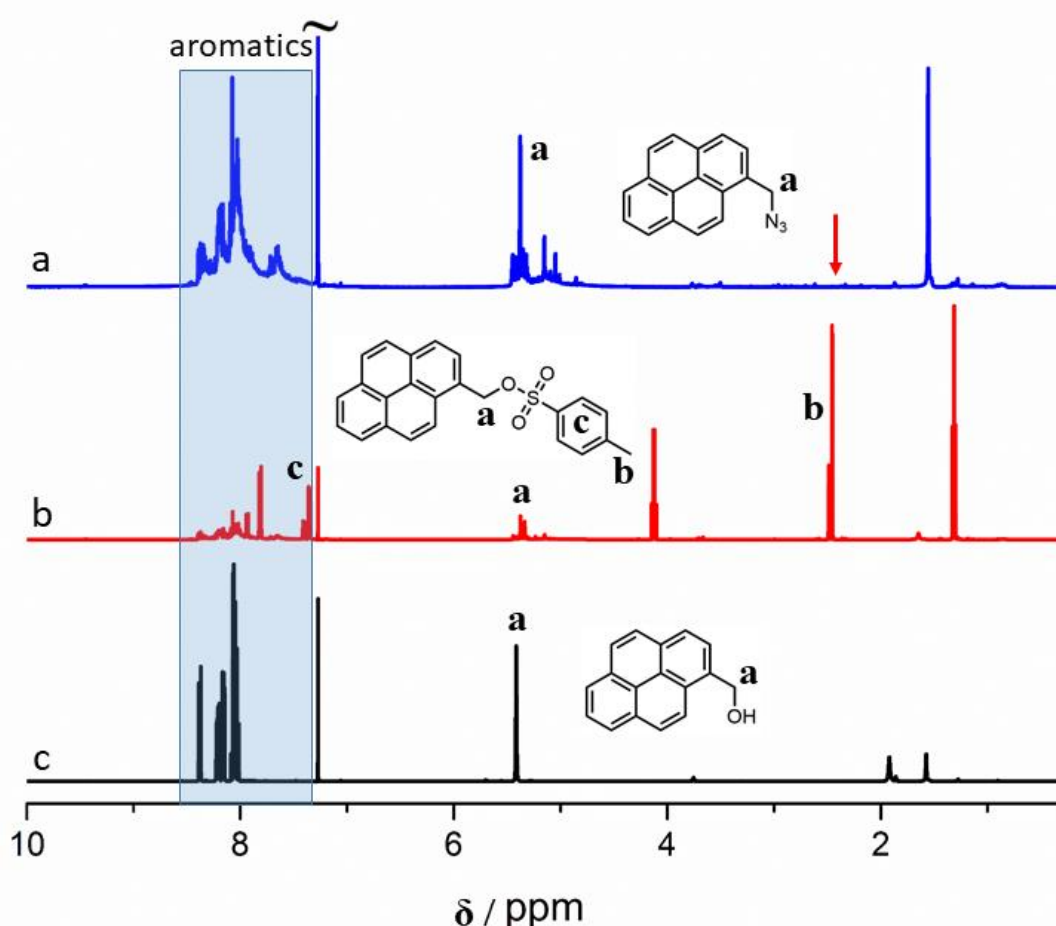
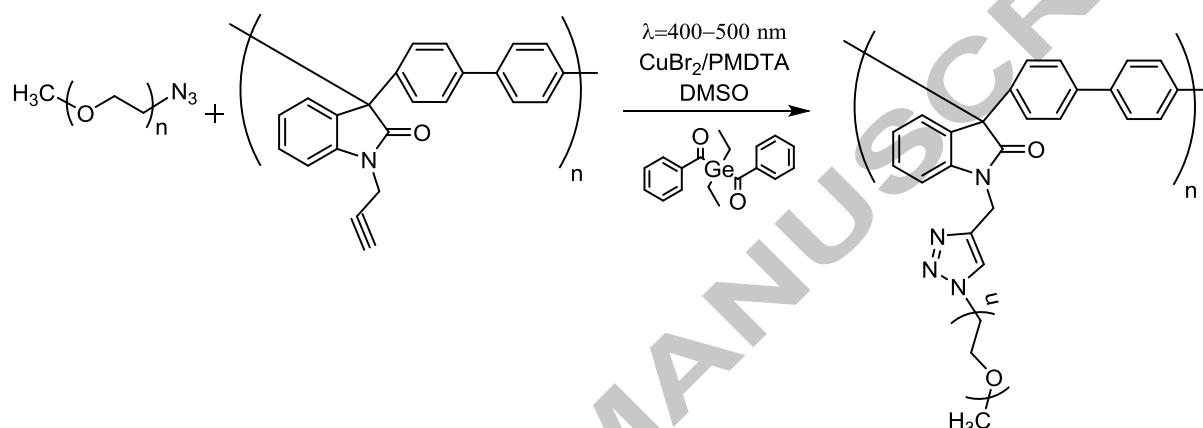


Figure 4. ^1H NMR spectra of Py-OH (c), Py-Ts (b) and Py- N_3 (a).

After the successful attachment of azide groups to the PEG, Py and DBP, photo-induced CuAAC reactions with alkyne side groups of POXI were conducted. PEG as the polymeric click component provided possibility for the spectral and molecular weight characterization of the ultimate grafted material because of its attractive solubility. Thus, photo-induced CuAAC of POXI-alkyne proceeded efficiently at 400-500 nm with PEG- N_3 in the presence of DBDEG, PMDETA and CuBr_2 resulting in the formation of graft copolymer (POXI-*g*-PEG) (Scheme 3). According to the NMR calculations, about 65% of the alkyne groups underwent successful ligation. Steric limitations and the high molecular weight of both components are

the obvious drawbacks for the quantitative reaction. The prolonged reaction time may be considered as one solution to increase the efficiency. However, the steric hindrance and molecular weight would still be effective. The solubility of the unreacted PEG segments provides possibility for easy separation and pure graft copolymers are obtained.

In this connection, it should be pointed out that the germyl radicals formed from the photolysis of DBDEG in the visible range readily reduces Cu(II) ions to Cu(I) species to trigger successful click reaction.[12]



Scheme 3. Photo-induced CuAAC reaction of POXI-alkyne with PEG-N₃.

Spectral, molecular weight and thermogravimetric investigations clearly confirm the success of the photo-induced click reaction. As shown in Figure 5, the ¹H NMR spectrum of the polymer display the specific signals of alkyne, azide and triazole. Alkyne signals at 2.24 ppm decreased but not completely disappeared. Also, the signal of -CH₂ next to the alkyne group at 4.60 decreased and a new signal emerged at 4.46 which corresponds to the clicked part of the structure. Additionally, the characteristic signals of triazole and PEG segment protons were observed at 7.65 ppm and around 3.3-3.8 ppm, respectively. Remaining alkyne moieties were detected by NMR and it is decent for further modification process of membrane.

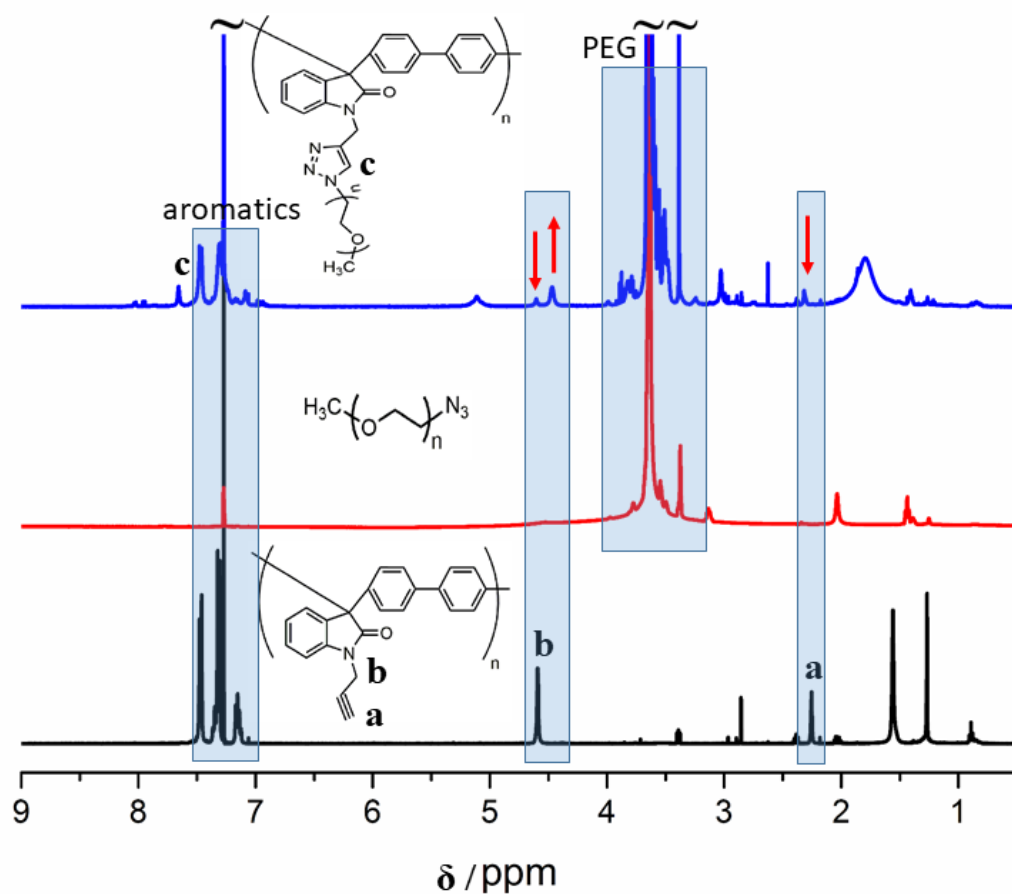


Figure 5. ^1H NMR spectra of POXI-alkyne, PEG-N₃, and POXI-g-PEG.

In the FT-IR spectrum of the graft copolymer showed no azide peak at 2100 cm^{-1} . The peaks around 1600 cm^{-1} associated with POXI segments were still present (Figure 6). Unreacted alkyne moieties were also detected around 3200 cm^{-1} .

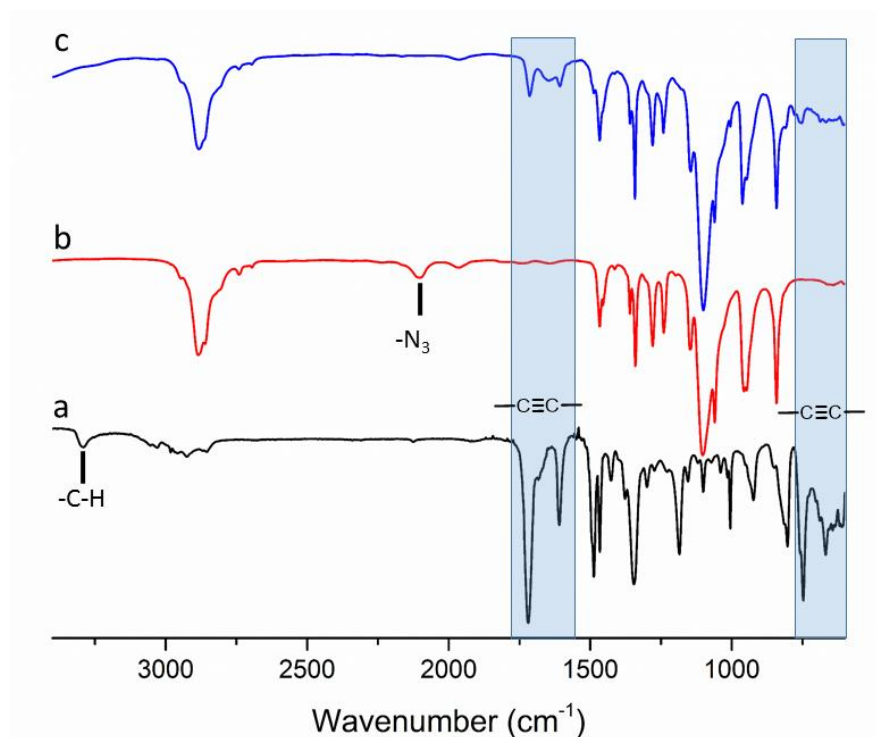


Figure 6. FT-IR spectra of POXI-alkyne (a), PEG-N₃ (b) and POXI-g-PEG (c).

The formation of graft copolymer was also evidenced by GPC analyses. The GPC traces of the precursor POXI-alkyne and the final graft copolymer are demonstrated in Figure 7. The clear shifts to higher molecular weight regions also confirms an efficient photo-induced click process.

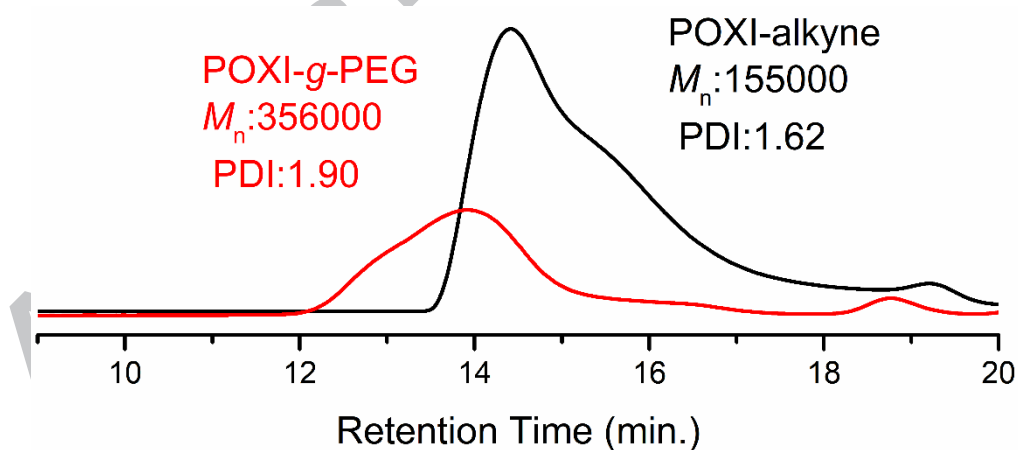


Figure 7. GPC traces of POXI-alkyne and POXI-g-PEG.

For further confirmation, thermal properties of the grafted polymer and its precursor polymers were investigated by DSC analyses. As can be seen from Figure 8, the melting temperature (T_m) of PEG segment appear at 48 °C which is slightly lower than that of the precursor PEG

(55 °C). The observed shift is in a good agreement with the literature value.[43] Notably, no detectable thermal transition was noted for the POXI segment. POXI has no measurable thermal transition such as T_m or glass transition (T_g) below its degradation temperature.

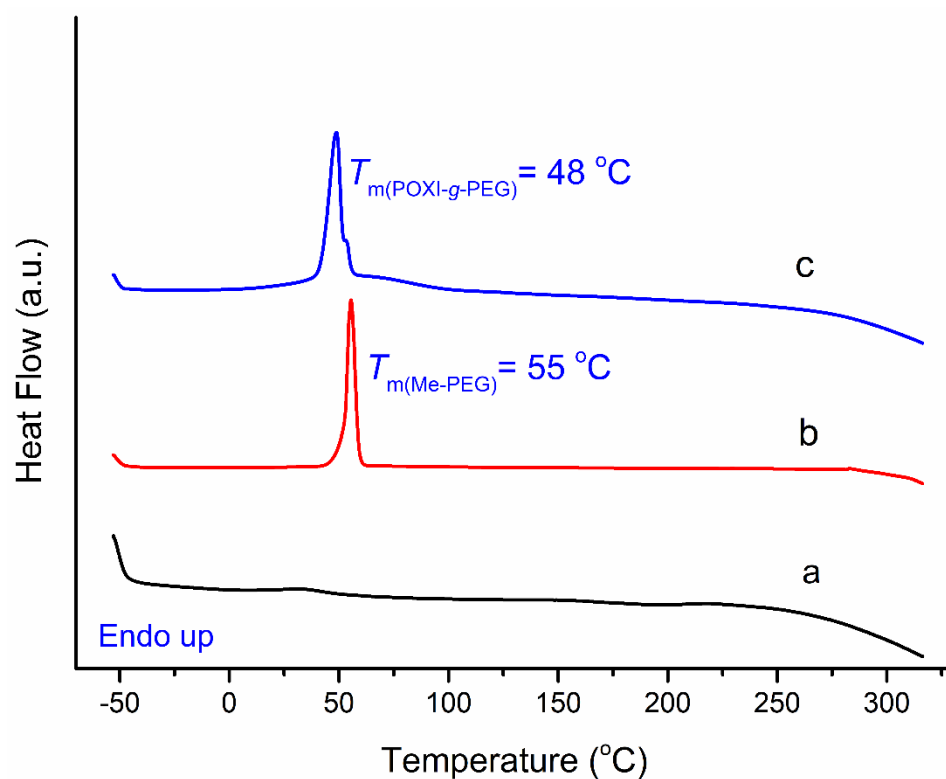
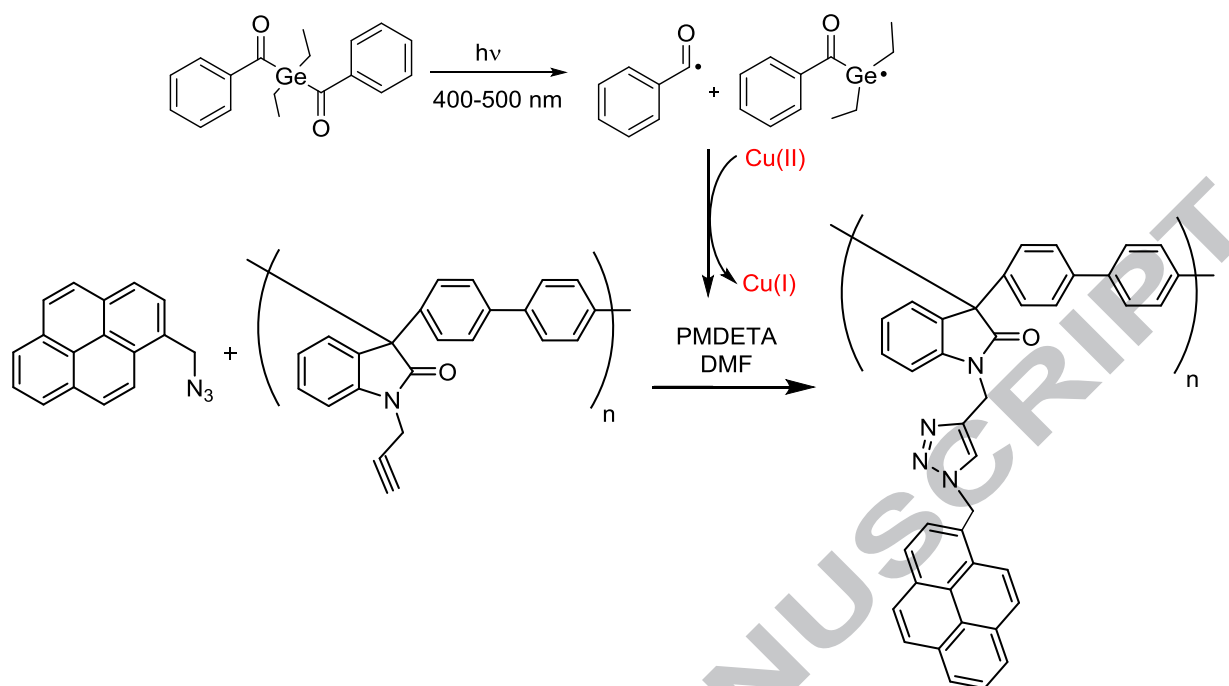


Figure 8. DSC thermographs of POXI-alkyne (a), Me-PEG (b) and POXI-g-PEG(c).

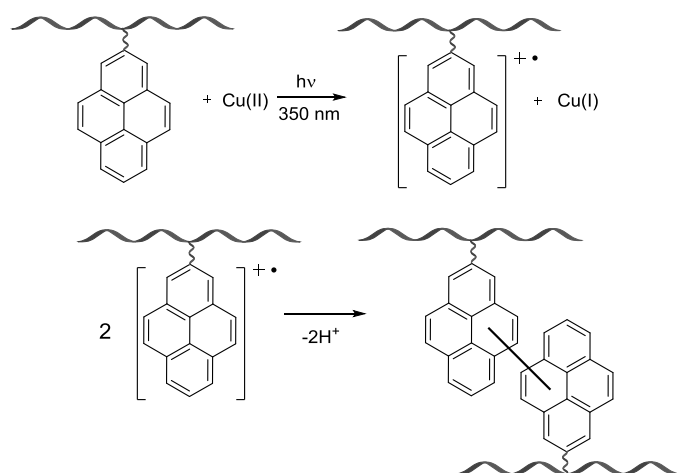
After the successful attachment of PEG segments to the polymeric POXI backbones, photo-induced CuAAC reactions with azide functional pyrene (Py- N_3) were conducted. The reason to select pyrene as a click component is that potential usage as semiconductors, photoresist materials and fluorescent probes[44]. Photo-induced functionalization of POXI-alkyne proceeded efficiently in the visible range with Py- N_3 in the presence of CuBr_2 , PMDETA and DBDEG as photoreducing agent to give side chain pyrene functional poly(oxindolebiphenylene) (POXI-Py) (Scheme 4).



Scheme 4. Photo-induced side chain modification of POXI with Py-N₃ by click chemistry.

The FT-IR spectrum of the obtained POXI-Py (Figure S4) exhibited characteristic peaks of both POXI and Py units. Notably, some alkyne groups remained unreacted. The incorporation of Py units was further confirmed by fluorescence measurements. In the fluorescence spectrum of POXI-Py, the excited state emission of pyrene moieties appears at around 380 and 400 nm (Fig. 9). The additional broad emission observed at 480-550 nm can be attributed to the excimer emission arising from the strong interactions of the excited pyrene moieties with those in their ground states present in close proximity. A similar behavior was observed with linear[45] and hyperbranched[46] polymers. Such fluorescence behavior can also be detected visually under UV light (Figure S5)

Since pyrene units absorb the light in UV region (Figure S3) and the excited state can participate in electron transfer reactions[47], it was anticipated that the reduction of Cu(II) can be achieved directly to trigger the CuAAC reaction without necessity of an additional photoinitiator. However, irradiation of POXI-alkyne and Py-N₃ at 350 nm in the absence of DBDEG resulted in the formation of insoluble material. This may result from coupling of Py units after reducing Cu(II) to Cu(I) (Scheme 5). Thus, both CuAAC and cross-linking reactions proceed concomitantly.



Scheme 5. Proposed reaction scheme for pyrene coupling.

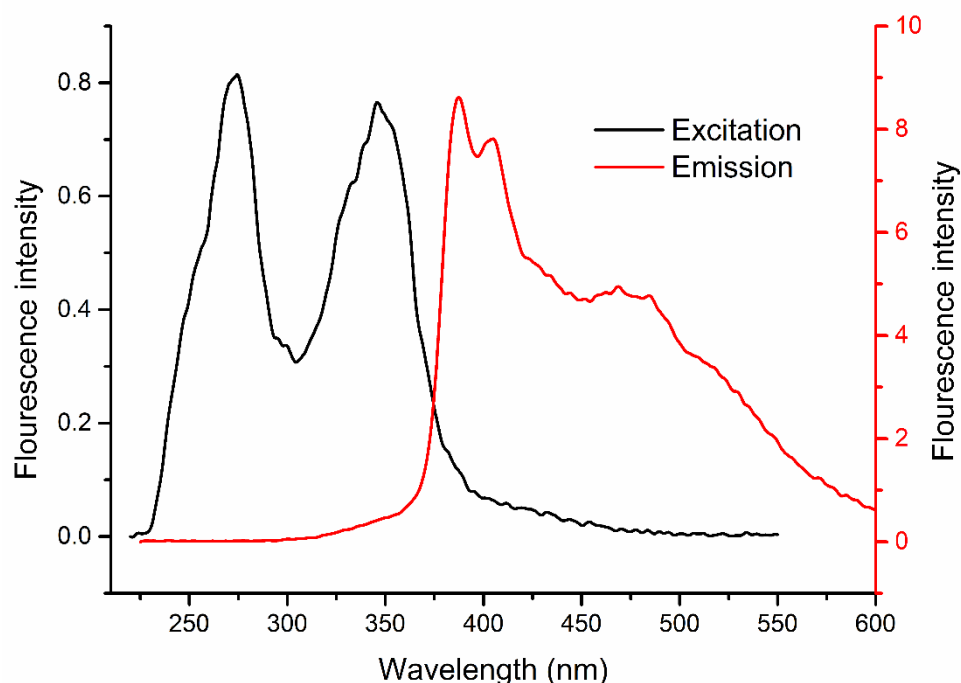


Figure 9. Fluorescence excitation and emission spectra of POXI-Py in CHCl₃ (with the excitation of 350 nm)

We have also tested potential cross-linking of POXI-alkyne by the described photoinduced CuAAC click reaction. For this purpose, the solutions of POXI-alkyne and bifunctional azide compound were irradiated in the visible range under similar experimental conditions. As can be seen from Figure 10, upon irradiation, the solution is rapidly converted into insoluble gel due to the successful intermolecular click reaction.

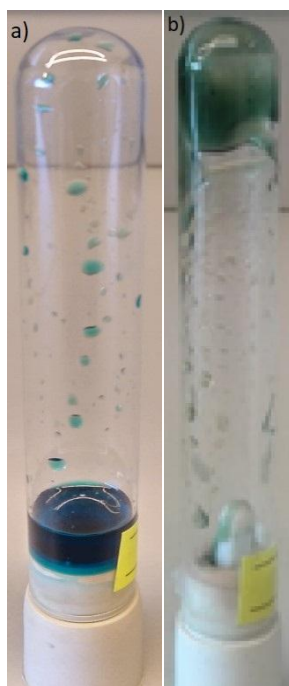


Figure 10. Photographs of clickable POXI solution which contains DAP, CuCl_2 , PMDETA and DBDEG in DMSO before (a) and after (b) click reaction under irradiation with visible light at 400-500 nm.

4. Conclusion

In summary, in this work a strategy was laid out via photo-induced CuAAC reactions to modify poly(oxindolebiphenylene). The course involves the synthesis of alkyne functional poly(oxindolebiphenylene), azide functional low molar mass and polymer components and photo-induced CuAAC reactions. The process allows to attach molecules or polymers with various mass and also provides cross-linked structure. The described photochemical process indicates the high efficiency to incorporate with a wide variety of specific groups and potential applications of orthogonal nature of photoinduced CuAAC. Compare to the existing methods[32], this approach also has the advantage of simplicity and applicability at low temperatures. The success of the protocol may lead new strategies for design and implementation in material and membrane science.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/.....>

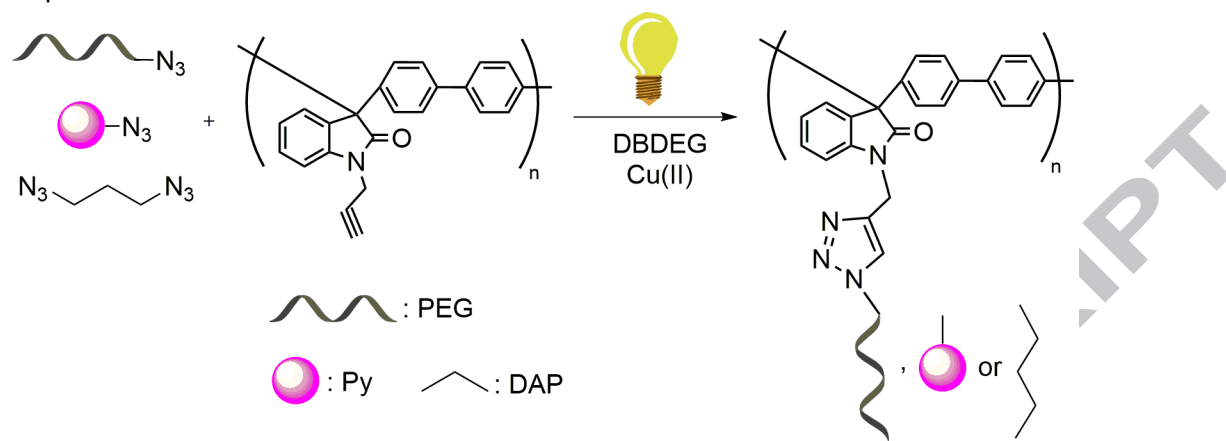
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Graphical abstract



Research highlights

- A novel strategy to obtain side chain modified poly(oxindole biphenylene) (POXI) by photoinduced copper(I)-catalyzed azide-alkyne cycloaddition (CuAAC) click reaction is described.
- An alkyne-functionalized poly(oxindolebiphenylene) (POXI-alkyne) and azid-functionalized poly(ethylene glycol) methyl ether (Me-PEG), 1-pyrenemethanol (Py-OH) and 1,3-dibromopropane (DBP) are synthesized.
- Modification of POXI confirmed by the spectral, (^1H NMR, FT-IR, Fluorescence), chromatographic (GPC) and thermal (DSC) investigations.