ELECTRONIC SUPPLEMENTARY INFORMATION

Synthesis of Ordered, Functional, Robust Nanoporous Membranes from Liquid Crystalline Brush-like Triblock Copolymers

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1. Materials

5-Norbornene-2-carboxylic acid (mixture of endo and exo, 98%), 4-dimethylaminopyridine (DMAP, 99%), N,N′-dicyclohexylcarbodiimide (DCC, 99%), Tris-(2-aminoethyl) amine (TAEA, 96%), N-Boc-ethanolamine (98%), 2-(Boc-oxyimino)-2-phenylacetonitrile (Boc-ON, 99%) trifluoroacetic acid (TFA, 99%), N-(3-Dimethylaminopropyl)-N′-ethylcarbodiimide hydrochloride (EDC,98%), DL-Dithiothreitol (DTT, 99%), Phenol (99%), 1,3-Di-Boc-2-(hydroxyethyl) guanidine, Sodium Nitrite $NaNO_2$ (99%), N,N-Dimethlyformamide (DMF, 99%) and Grubbs catalyst second generation are purchased from Aldrich and used without further purification. Grubbs catalyst is modified from second generation $(H_2IMes)(pyr)_2(Cl)_2RuCHPh$ (mG2)[1] as reported in literature. Dry methylene chloride (CH_2Cl_2, 99.8%) and ethyl vinyl ether (EVE, 99%) are purchased from Acros Organics.

Methods

^1H NMR spectroscopy is performed on Bruker DMX 500 MHz NMR spectrometer with $CDCl_3$ as solvent at room temperature. Mass spectrum is obtained with Micromass Quattro-II triple quadruple mass spectrometer equipped with an electrospray ionization (ESI) positive ion mode source. Gel permeation chromatography (GPC) is performed using a Waters 1515 coupled with a PL-ELS1000 evaporative light scattering (ELS) detector and a Waters 2487 dual wavelength absorbance UV-Vis detector with tetrahydrofuran (THF) as eluent and polystyrene (PS) standards for constructing a conventional calibration curve. Differential scanning calorimetry (DSC) is performed on TA-2920 instrument (Q-200 series) calibrated with an Indium standard. The amount of sample is 5-10 mg and scanning rate is 10 °C/min. Phase transition temperatures are determined by first cooling cycle using Universal Analysis software. Fourier transform infrared (FTIR) spectra are recorded on a Nicolet Magna 560 FTIR spectrometer using the KBr pellet technique.

Small angle X-ray scattering (SAXS) is performed on a pin-hole collimated Rigaku SMAX3000 instrument configured with CuKα radiation (1.542 Å) produced by a micro-focus source. The beam diameter on the sample plane is 1 mm and the scattered intensity is recorded on a gas-wire electronic area (2D) detector. The area detector has a resolution of 1024 × 1024 pixels and is located at a distance of ~80 cm from the sample center permitting access of scattering vectors ranging from 0.015 to 0.22 $Å^{-1}$. Silver behenate (*d*-spacing=58.38 Å) is used to calibrate the SAXS diffraction patterns. Wide-angle X-ray scattering (WAXS) patterns is obtained on a Fuji image plate and the q-calibration is done using Si (111) with a d-spacing of 3.1355 Å. 1D representation of the scattered intensity against scattering vector q, where $q = (4\pi/\lambda) \times \sin\theta$, ($2\theta$ is the scattering angle) is obtained using MATLAB routines (Rigaku). Scanning electron microscope (SEM) images of all samples are recorded using an FEI Teneo LVSEM equipped with an ETD detector with an accelerating voltage 15 kV. The film samples (≈ 240 µm thick) were prepared by compression molding and sputter coated with a thin gold conductive layer before imaging.

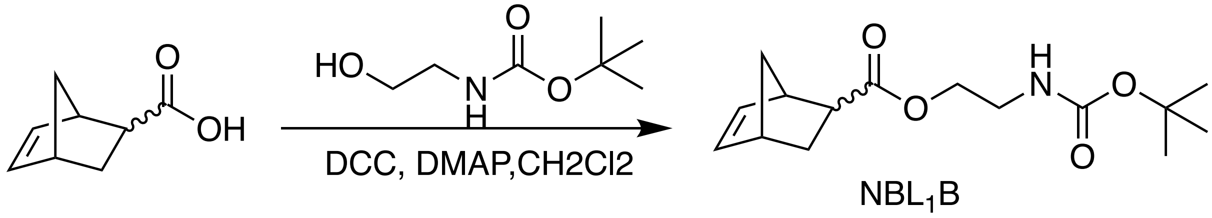
2. Synthesis Protocols

2.1. Synthesis of norbornenyl end-functionalized poly (D, L-lactide) (NBPLA2k)

NBPLA2k macromonomer is synthesized as previously reported with slight modification.[2] In summary, a flame dried schlenk tube is charged with 5-norbornene-2-methanol (*endo/exo* = 63/37) (574 mg, 4.63 mmol), D,L-lactide (8.0 g, 55.51 mmol), tin (II) 2-ethylhexanoate (37.5 mg, 0.093mmol) and a magnetic stir bar. Using a laboratory schlenk line, the reaction tube is evacuated and backfilled with nitrogen for 4 times. Then, the reaction tube is placed in oil bath, and stirred for 12 h at 100 °C. Afterward, the reaction mixture is cooled to room temperature, diluted with THF, precipitated into cold acidified methanol, and dried in vacuum oven overnight at room temperature. 3.7 g, yield = 41.0%, M_n (^{1}H NMR) = 1868 g/mol, M_n (GPC-ELSD) = 2817 g/mol, PDI = 1.12.

Synthesis of NBL_1B

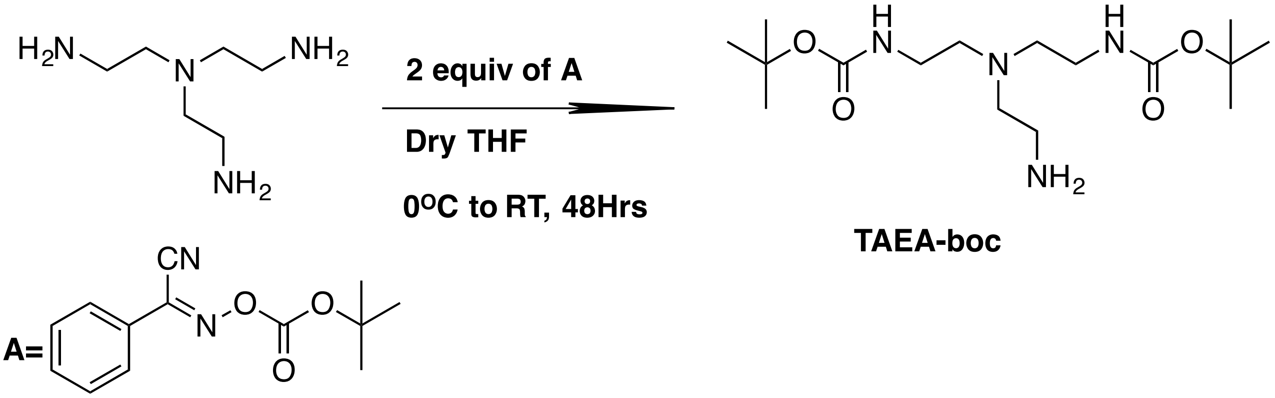
N-Boc-ethanolamine (10.26 g, 63.7 mmol) is transferred dropwise to a vigorously stirring solution mixture of 5-Norbonene-2-carboxylic acid (8.0 g, 58 mmol), DCC (11.94 g, 58 mmol) and DMAP (1.49 g, 12.2 mmol) in 25 mL of chloroform at 0 ˚C in a round bottom flask. After 30 minutes of stirring at 0 ˚C, the reaction is allowed to warm to room temperature and stirred for three hours. After three hours of reaction, the mixture is diluted with chloroform and filtered. The filtered mixture is then transferred to a separating funnel, washed with distilled water (2 x 100 mL), 0.5 M sodium bicarbonate (2 x 100 mL) and 0.5 M sodium citrate tribasic dehydrate (100 mL). The organic phase is dried over $MgSO_4$ and resultant product is filtered, concentrated then purified on a silica column eluting with 3:2 ethyl acetate/hexane. The purified product is concentrated and precipitated in vigorously stirring hexane then dried in a vacuum oven overnight obtaining a white solid (**L_1B,** 7.5 g, 46.1% yield). ESI-MS: calculated $\{MH\}^{+}$= 282.1705, obs. = 282.1713



Scheme S1: Synthesis of NBL$_1$B.

2.2. Protection of tris-(2-aminoethyl)amine to form (Bis-(2-(tert butoxycarbonylamino)-ethyl)-(2-aminoethyl)amine; TAEA-Boc)

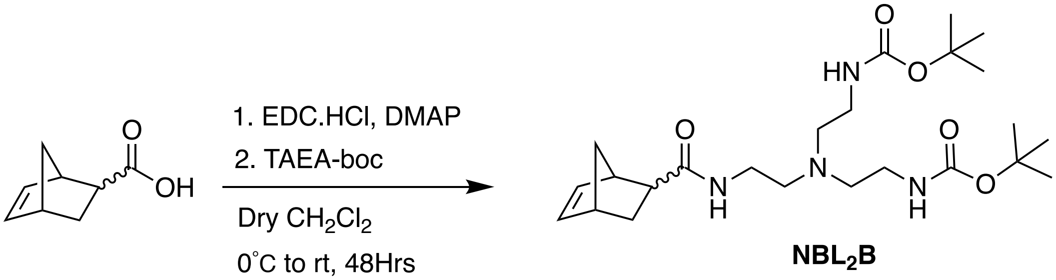
The synthesis of TAEA-Boc follows a slightly modified procedure previously reported by Friederike *et.al.*[3] A solution of 1.49 g of Tris-(2-aminoethyl) amine (TAEA) in 40 mL of THF is cooled to 0 ºC. 5.31 g of 2-(Boc-oxyimino)-2-phenylacetonitrile is dissolved in 60 mL of dry THF and added to the solution dropwise. The reaction is left to warm up to room temperature and let to go on for 48 hrs. The product is purified by column chromatography using Dichloromethane/ methanol: TEA (95:5, 1% v/v) with a 65% yield.



Scheme S2: Formation of TAEA-boc: (Bis-(2-(tert-butoxycarbonylamino)ethyl)-(2-aminoethyl)amine).

2.2.1. Synthesis of NBL$_2$B

N-(3-Dimethylaminopropyl)-N′-ethylcarbodiimide hydrochloride is used as the coupling agent of choice. Generally, the reaction takes place in an ice bath at 0 ºC until the first two reagents are added and then left to gradually warm up to room temperature. Typically, 877.28 mg (6.35 mmol) of 5-Norbornene-2-carboxylic acid are charged into a round bottomed flask and dissolved in 10 mL of dry dichloromethane. Nitrogen gas is purged into the flask as it stirs for 5 minutes. Meanwhile, in a separate vessel, 1.22 g (6.35 mmol) of EDC.HCl is dissolved in a minimum amount of dichloromethane and then added dropwise into the flask under nitrogen. 70.52 mg (0.577 mmol) of 4-dimethylaminopyridine (DMAP) are added immediately after EDC.HCl. The reaction is allowed to proceed for 20 minutes when 2.0 g (5.77 mmol) of TAEA-Boc is added into the flask under nitrogen atmosphere. The reaction is allowed to warm up to room temperature and then allowed to take place for 48 hrs. The crude formed is purified by washing it with DI water (2 x100 mL) and extracted using DCM. The crude product is then dried using MgSO$_4$, concentrated and purified using silica gel with ethyl acetate/hexane/methanol as the eluent (6:3:1). Yield 75%.

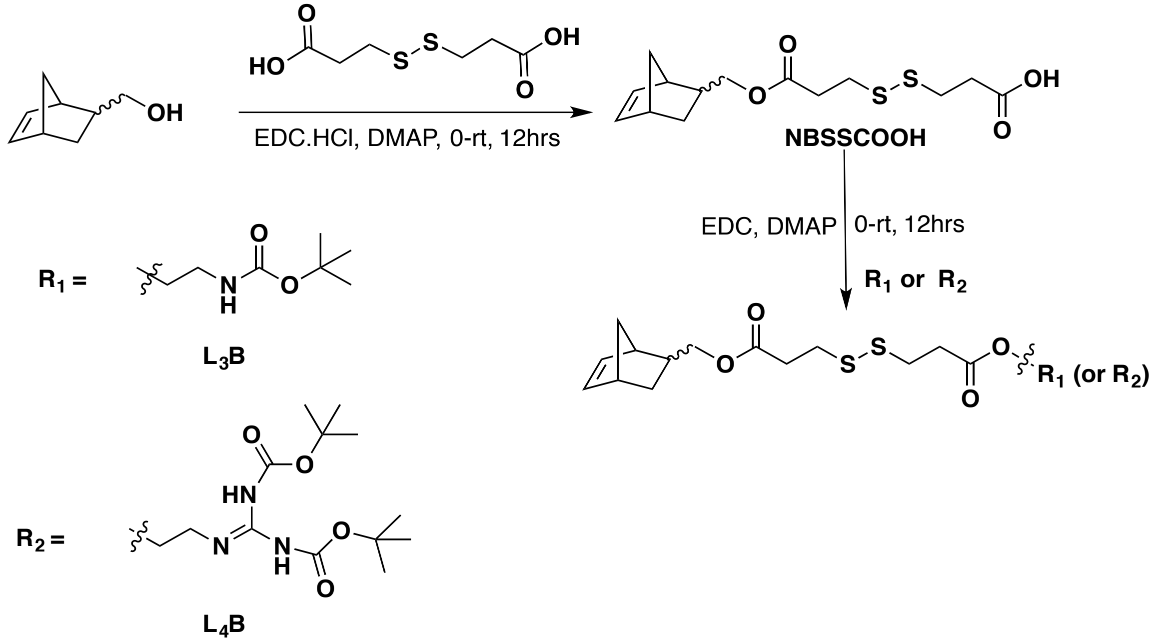


Scheme S3: Synthesis of NBL$_2$B

3.4. Synthesis of NBL$_3$B and NBL$_4$B

NBL$_3$B was prepared by the EDC.HCl/DMAP catalyzed esterification of excess carboxylic acid from 3,3'-Dithiodipropionic acid with 5-Norbornene-2-methanol. A solution of EDC.HCl (9.26 g, 48.3 mmol) in 15 mL dichloromethane is added dropwise to a solution of 5-Norbornene-2-methanol (1.5 g, 12.1 mmol), 3,3'-Dithiodipropionic acid (10.2 g, 48.3 mmol) and DMAP (0.74 g, 6.0 mmol) in 20 mL dry dichloromethane at 0 ºC. The reaction is allowed to stir overnight at room temperature. The reaction mixture is filtered and washed using sodium bicarbonate (2 x 200 mL). The organic layer is dried over $MgSO_4$, concentrated and purified further using silica gel column with DCM/MeOH (95:5) as eluent. The pure fractions are concentrated under vacuum to afford a light-yellow oil of NBSSCOOH (Scheme S4).

Using NBSSCOOH both NB-SS-NH_2Boc and NBSSdiNH_2DiBoc are synthesized. Briefly in a round bottom flask at 0 °C either N-Boc-ethanolamine (2 g, 12.4 mmol) or 1,3-Di-Boc-2-(hydroxyethyl) guanidine (1.5 g, 4.7 mmol), dissolved in 10 mL DCM is charged. This is followed with addition of DMAP and NBSSCOOH and purging of nitrogen for 5 minutes. A solution of EDC.HCL is then added dropwise to the reaction mixture at constant stirring. After 30 minutes of stirring at 0 ºC the reaction is allowed to warm to room temperature to run overnight. The crude product is filtered, washed with sodium bicarbonate (2 x 100 mL) and H_2O (2 X100), then purified further using silica gel column with hexane/ethyl acetate (70:30).



Scheme S4: Synthesis of NBL_3B and NBL_4B.

2.6. Synthesis of PTBCs.

A representative ring-opening metathesis polymerization (ROMP) of functionalized norbornene monomers is described as below. NBCB12 (500 mg, 1 mmol) is added to a scintillation vial equipped with a magnetic stir bar and a rubber septum. To this vial, 10 mL of CH_2Cl_2 is added and purged with nitrogen for 5 min. In a separate vial, mG2 (33 mg, 0.046 mmol) is dissolved in CH_2Cl_2 (3 mL) and purged with nitrogen for 3 min. Then, these two solutions are combined and reaction is allowed for 15 min at room temperature. After the first polymerization is complete, pre-purged CH_2Cl_2 solution containing L_2B (181 mg, 0.09 mmol) is added, and stirred for another 25 min. After the second polymerization is complete, pre-purged CH_2Cl_2 solution containing NBPLA2k (181 mg, 0.09 mmol) is added, and stirred for another 25 min. Then, the reaction is terminated by adding excess ethyl vinyl ether (EVE). The resulting triblock polymer LC73-L_2B5-PLA22, is precipitated into methanol, filtered, and dried in vacuum oven overnight at room temperature. M_n (GPC-ELSD) = 15.7 kg/mol, PDI = 1.07, Table 2 in the main manuscript.

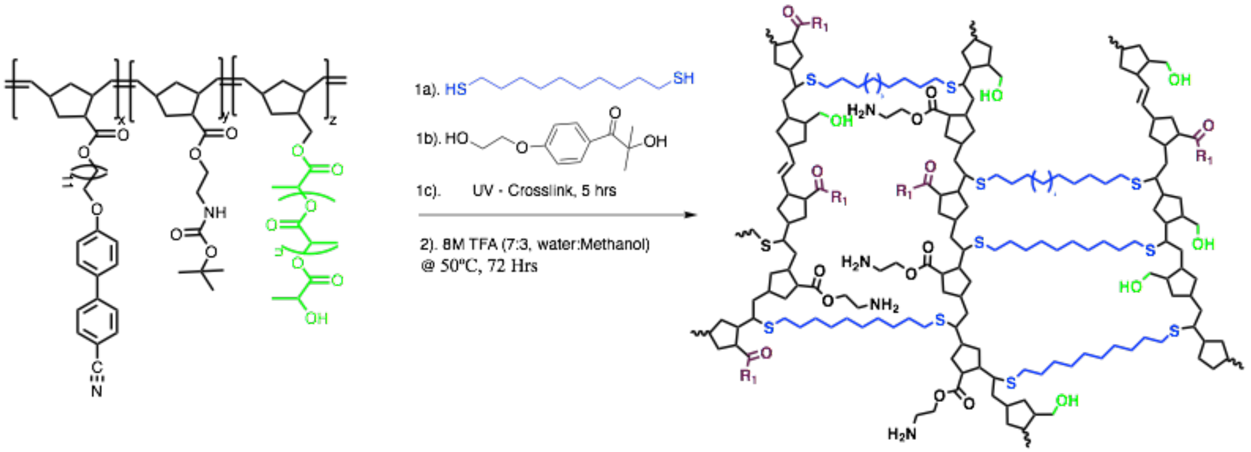
3.0 Preparation of nanoporous membranes (NPM)

3.1. Representative PTBC crosslinking procedure

A representative nanoporous membrane is made as follows. 100 mg of amine protected triblock copolymer (**LC73-L_1B5-PLA20**), 5 mg of 2-Hydroxy-4′-(2-hydroxyethoxy)-2-methylpropiophenone, and 12 mg of 1,10-decanedithiol are weighed in a vial covered in aluminum foil. 1 mL of THF is added to the vial to dissolve the contents. The solvent is then evaporated completely and a film compression molded at 85°C and quenched to room temperature (film thickness=240µm). This is followed by UV-crosslinking for 5 hours rendering a crosslinked film. The crosslinking density 28% as established by gel fraction in THF The film is then crosslinked under UV for 5 hours yielding flexible film with crosslinking density 28% as established by gel fraction in THF.

3.2 Deprotection and Etching of crosslinked triblocks

A representative simultaneous deprotection and etching of crosslinked triblocks is carried out as follows: 200 mg of crosslinked film sample prepared as described in 3.1 above, LC73-L_1B5-PLA22, is immersed in a solution of 8M TFA prepared in 7:3 (water : methanol) mixture and maintained at 50 ºC for 3 days. After three days, the nanoporous membrane thus formed is washed with copious amount of distilled water to remove any residue left after deprotection and etching. It is then immersed in methanol for 30 minutes and dried overnight. The sample is characterized by FTIR and through NMR.



Scheme S5: Schematic reactions showing preparation of nanoporous membrane (NPM-1).

3.3. Confirmation of pore functionalization

3.3.1. Disulfide bond cleavage

100 mg of non-crosslinked polymer (LC72-L_4B8-PLA20) is charged into a vial and dissolved in ethyl acetate. The vessel is stirred under nitrogen for 5 minutes. In a separate vial, 5.864 mg of dithiothreitol (DTT) is dissolved in ethyl acetate and added into the reaction vessel followed by 0.3mL of Et_3N. The reaction is stirred under nitrogen for a further 10 minutes and left to run for two hours. On completion, the contents are concentrated and precipitated into methanol. Traces of DTT are removed by Soxhlet extraction (24 hrs) in methanol. The pure cleaved polymer is dissolved using minimal amount of DCM, re-precipitated in methanol and dried overnight in a vacuum oven. The product is analyzed by FTIR and ^1H NMR.

3. Characterization Results

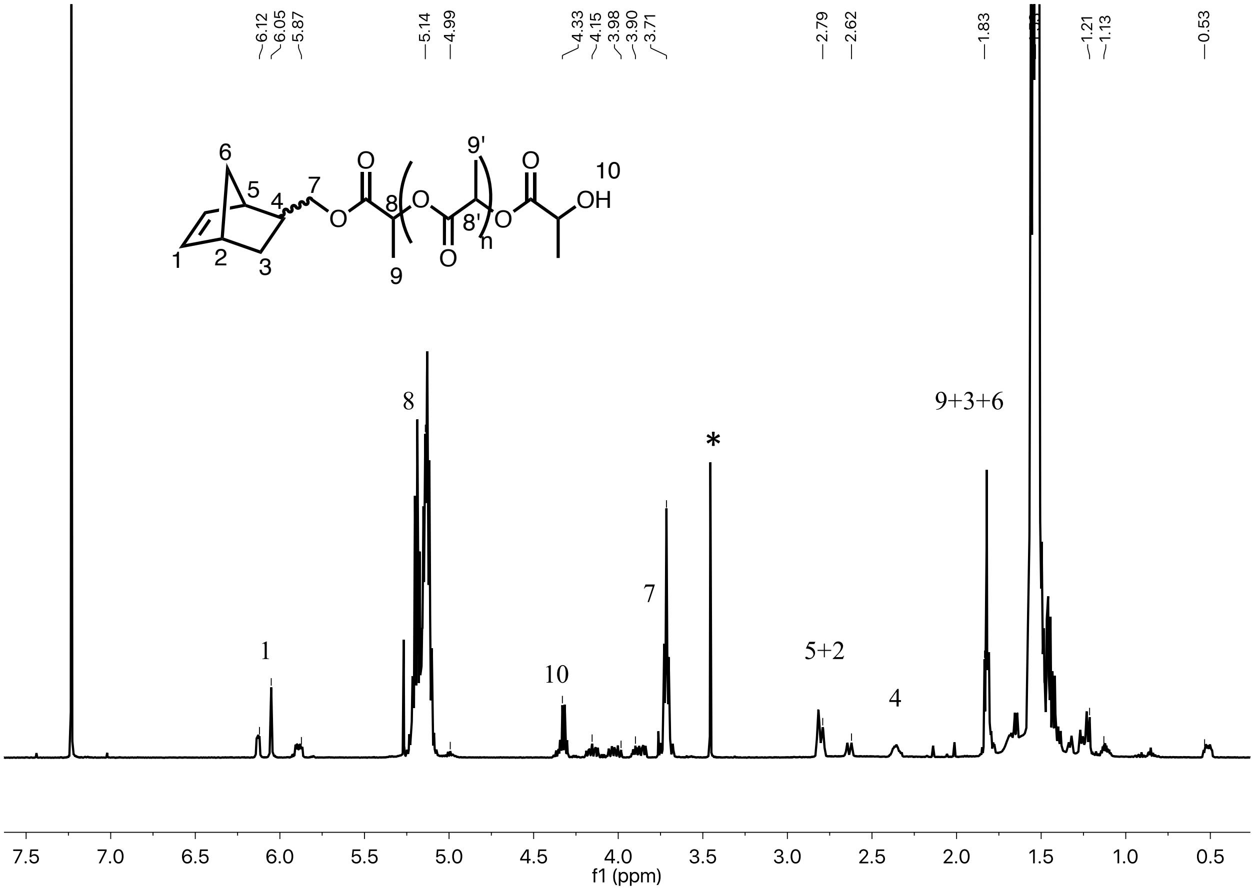


Figure S1: Representative ^{1}HNMR of NBPLA in $CDCl_3$ at room temperature.

(* Methanol)

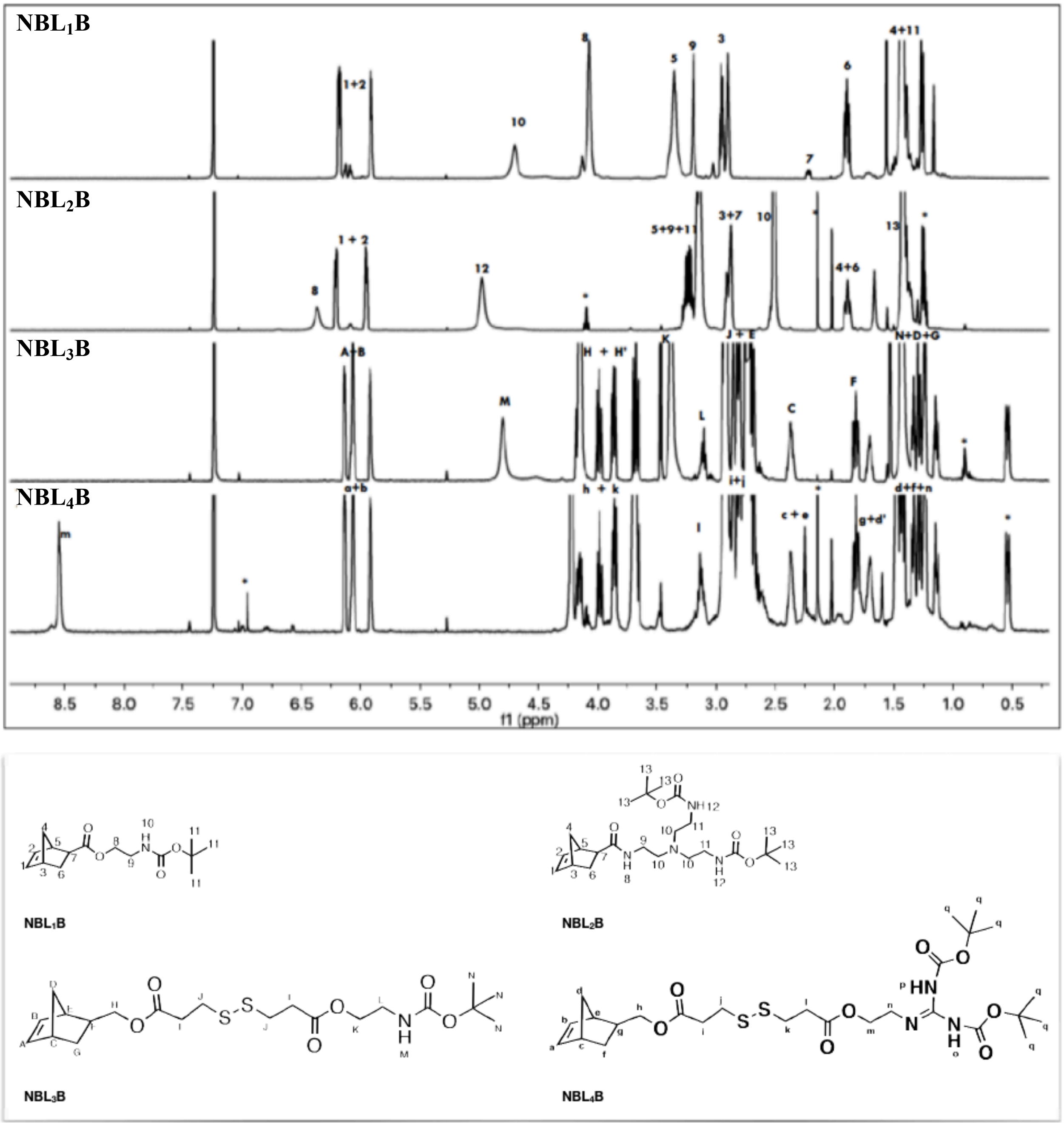


Figure S2: ^{1}H NMR for the new monomers in $CDCl_3$ at room temperature.

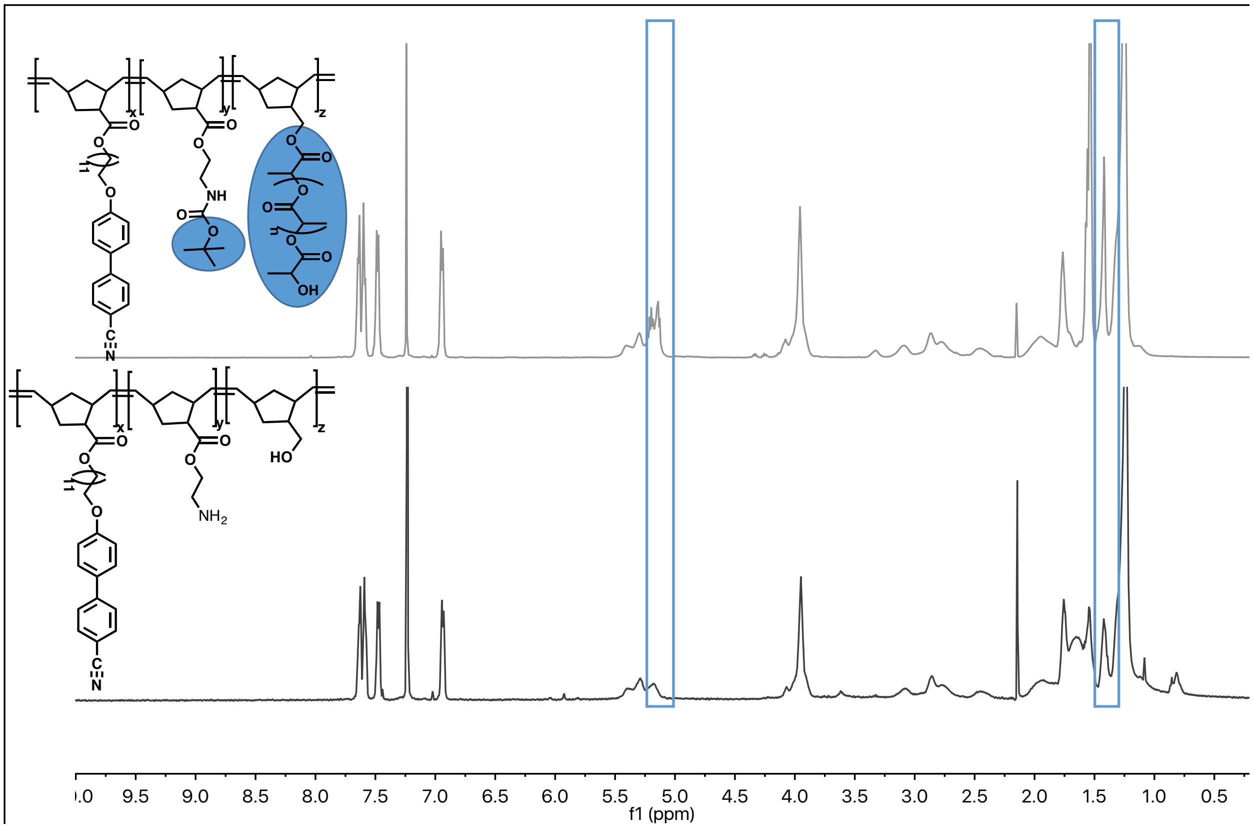


Figure S3: Representative ^{1}H NMR of LC73-L$_1$B5-PLA22 (above) and a nanoporous polymer (below). The highlighted peaks indicate the peak transitions due to removal of both boc group and etching of PLA unit.

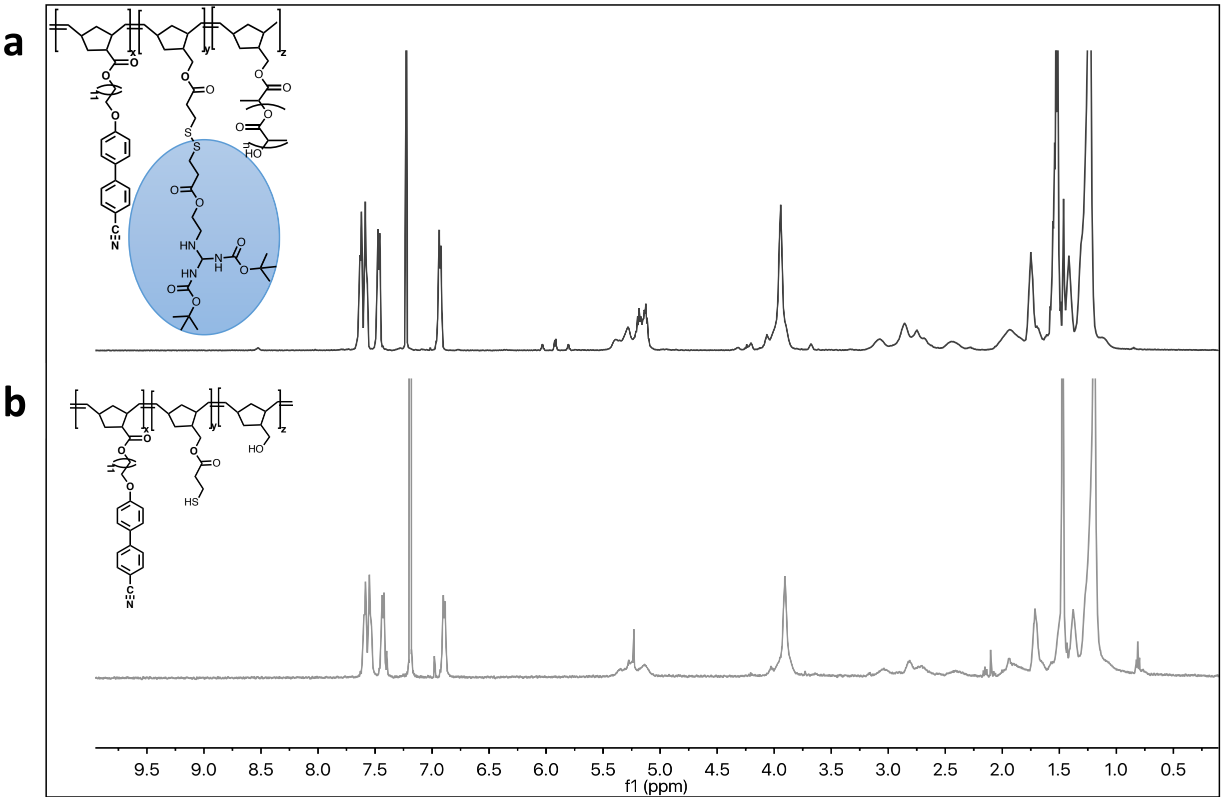


Figure S4: Representative ^{1}HNMR of LC72-L$_4$B8-PLA20 (a) before cleavage of -SS- bond and (b) after cleavage.

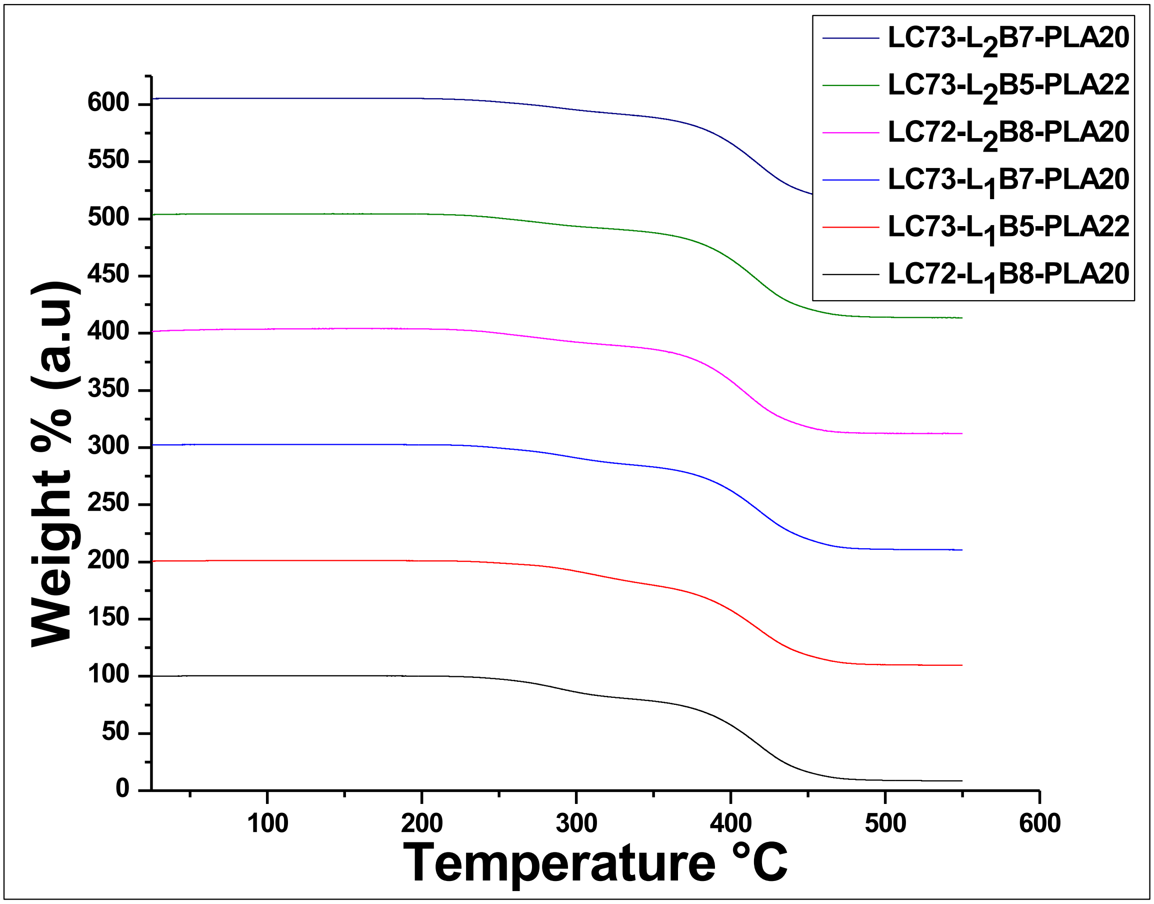


Figure S5. TGA of select PTBCs.

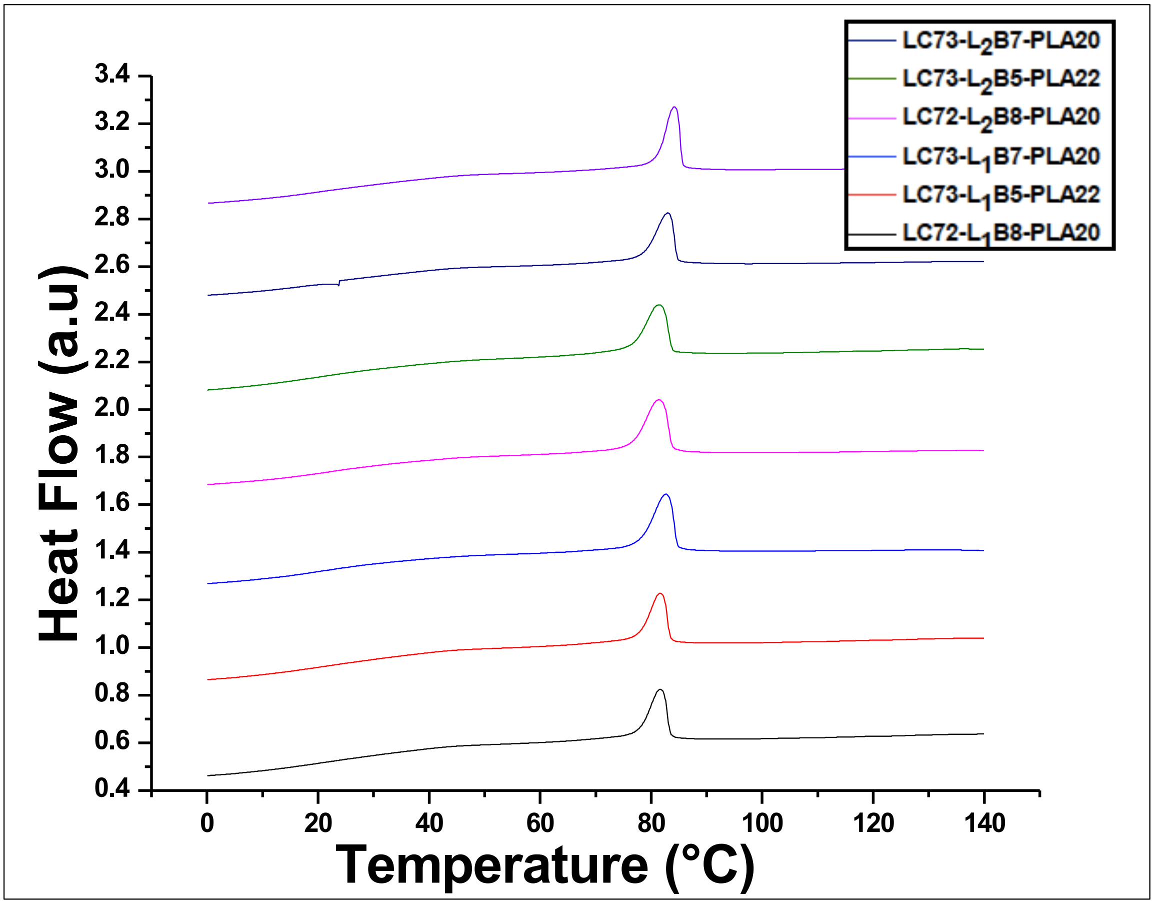


Figure S6: DSC cooling traces of the polymers. Glass transition temperature of selected PTBCs appear ~25-30°C.

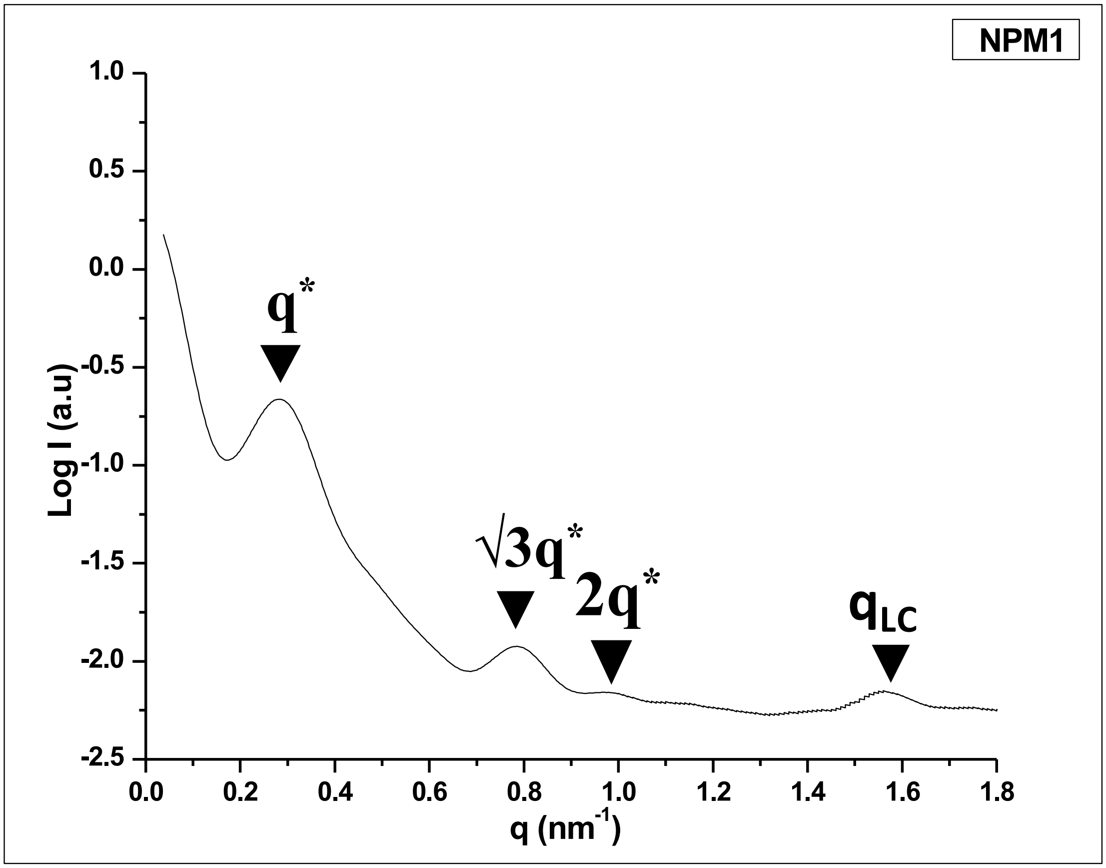


Figure S7: SAXS for nanoporous membrane NPM-1. The morphology of the nanoporous membrane is confirmed to be cylindrical.

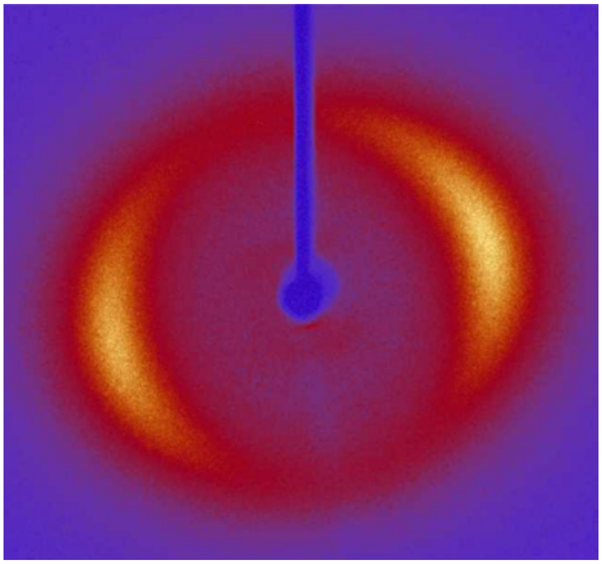


Figure S8: 2D WAXS pattern of nanoporous membrane, NPM-1, which in conjunction with SAXS represent the lateral spacing of LC mesogens confirm ordered membrane.

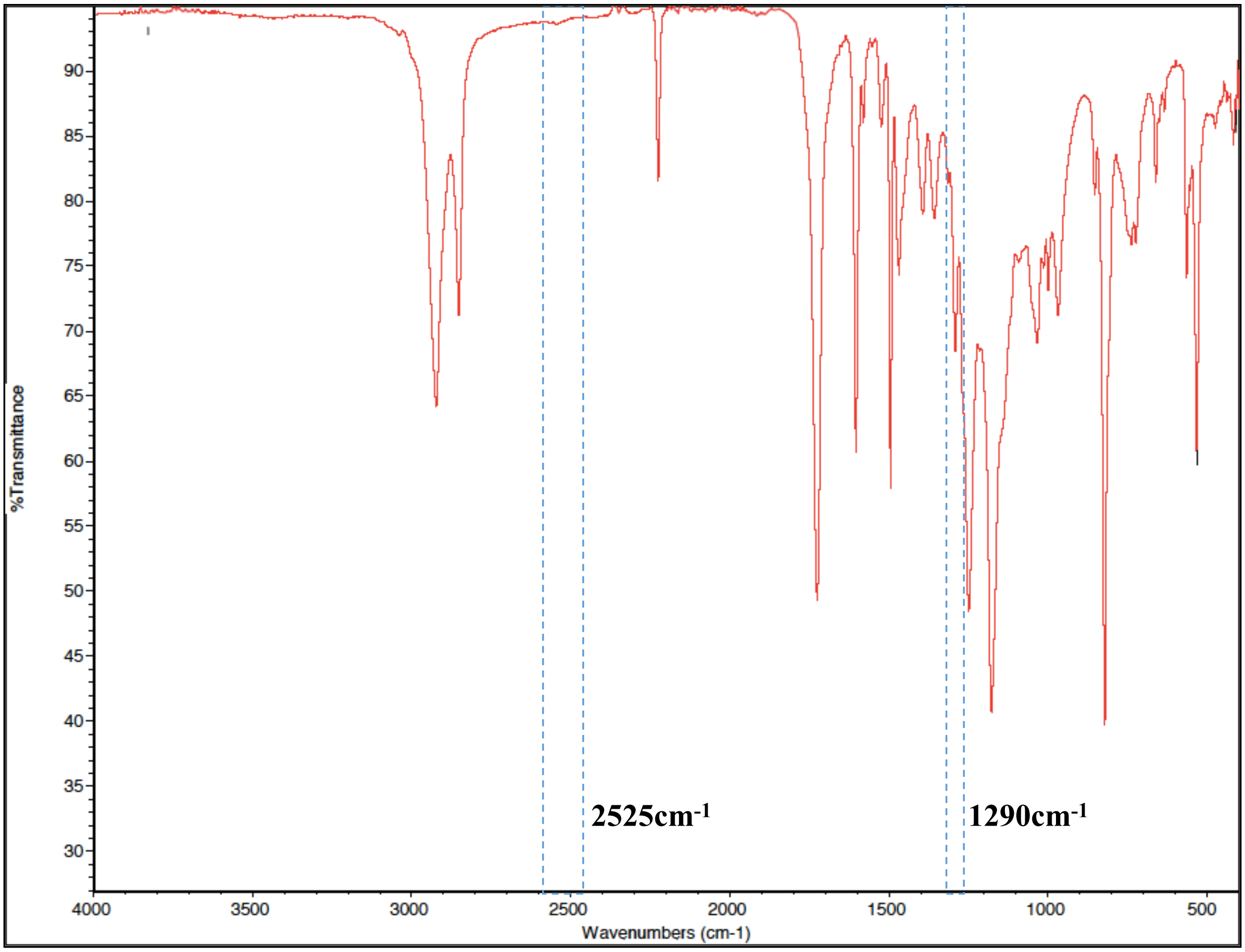


Figure S9: Representative FTIR of LC72-L48-PLA20 after cleavage of -SS- bonds.

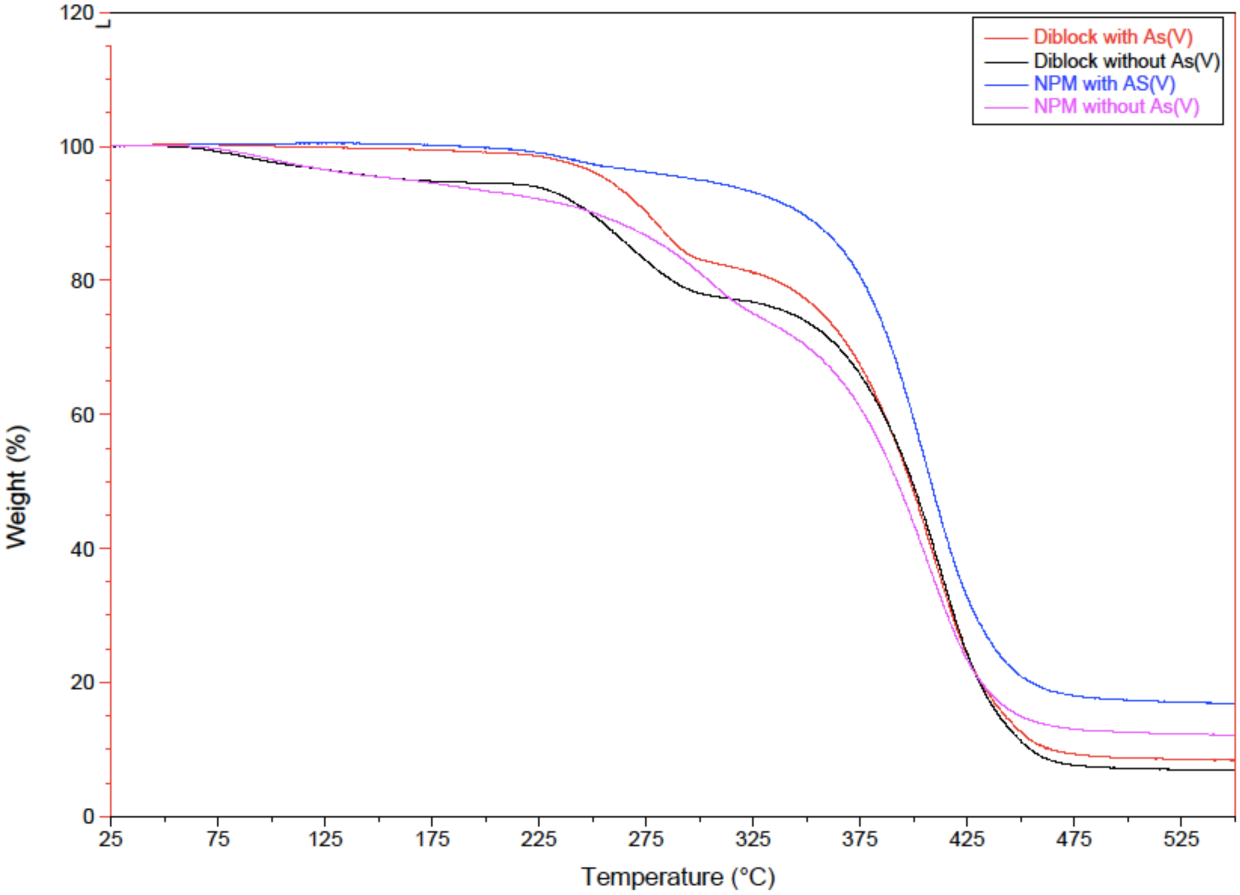


Figure S10: TGA traces of effect of As (V) adsorption by nanoporous membrane compared to diblock control samples.

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1. S.-k. Ahn, P. Deshmukh and R. M. Kasi, *Macromolecules*, 2010, **43**, 7330-7340.
2. P. Deshmukh, M. Gopinadhan, Y. Choo, S.-k. Ahn, P. W. Majewski, S. Y. Yoon, O. Bakajin, M. Elimelech, C. O. Osuji and R. M. Kasi, *ACS Macro Letters*, 2014, **3**, 462-466.
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