

## Modular Polymerized Ionic Liquid Block Copolymers Membranes for CO<sub>2</sub>/N<sub>2</sub> Separations

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### Synthesis of 1-thioacetyl-11-methacroyl undecane (TAMAUD)

In a 100 mL flask 12.25 g of 11-bromo undecanol (48.8 mmol), 50 mL dry dichloromethane, and 7.2 mL NEt<sub>3</sub> (51.6 mmol), were combined and cooled in an ice bath. Thioacetic acid (3.64 mL, 51.6 mmol) was then added dropwise in 15 mL of dry dichloromethane. The ice bath was subsequently removed and the reaction stirred for 24 hours. Afterwards, all of the volatile components were removed by rotary evaporation. Diethylether was added and the NEt<sub>3</sub>·HCL salt filtered off. The supernatant liquid was washed twice with water, dried with magnesium sulfate, and the solvent evaporated to give a yellow oil.

The resulting liquid was then combined with 7.2 mL of triethylamine (51.6 mmol) and 30 mL dry dichloromethane. The flask was then cooled in an ice bath while 5.0 mL of methacryloyl chloride (51.2 mmol) was added dropwise in 13 mL of dry dichloromethane. A precipitate instantly formed, but the reaction was allowed to proceed overnight. Afterwards, all of the volatile components were removed by rotary evaporation. Diethylether was added and the NEt<sub>3</sub>·HCL salt filtered off. The resulting liquid was washed with water, saturated sodium bicarbonate, and brine. It was then dried over magnesium sulfate, and the excess solvent evaporated. Yield 91 % for both steps. <sup>1</sup>H NMR (300 MHz, CHLOROFORM-d) δ ppm 1.02 - 1.37 (m, 16 H) 1.49 - 1.77 (m, 4 H) 1.92 - 1.99 (m, 3 H) 2.33 (s, 3 H) 2.81 - 2.91 (m, 2 H) 4.15 (t, J=6.77 Hz, 2 H) 5.53 - 5.58 (m, 1 H) 6.09 - 6.13 (m, 1 H)

### PPG Macro CTA

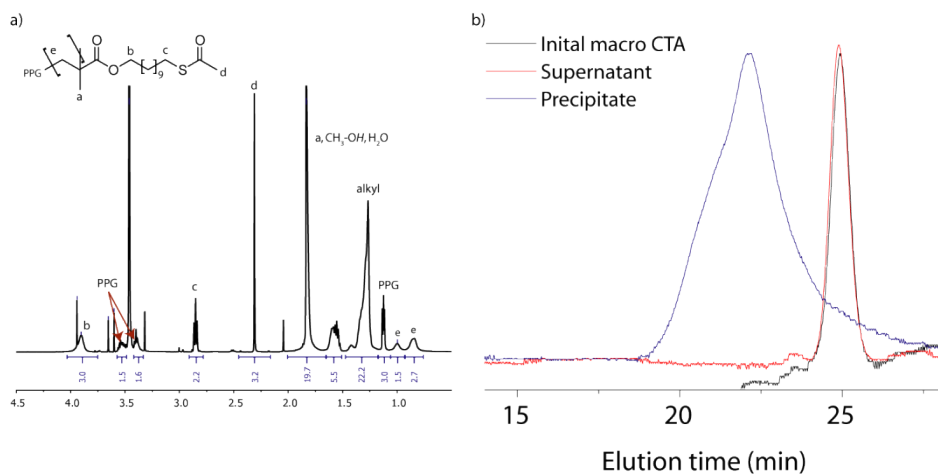
In a dried flask 0.0257 g 4-dimethylaminopyridine (0.21 mmol), 0.3670 g 4-cyano-4-(phenylcarbonothioylthio)pentanoic acid (1.3 mmol), 2.50 g 4 kDa PPG (0.63 mmol), and 30 mL anhydrous dichloromethane were combined. A solution of 0.3385 g N,N'-dicyclohexylcarbodiimide (1.6 mmol) in 8 mL dry dichloromethane was then added dropwise. A precipitate formed within a few minutes, but the reaction was allowed to proceed overnight. The following day the solvent was evaporated and the material re-dissolved in 30 mL of di-ethyl ether. The dicyclohexylurea byproduct was filtered off. Finally, the mixture washed three times with water (15 mL), and dried on vacuum line. Yield 88%

### PMMA Macro CTA

Methyl methacrylate was de-inhibited by passing it over a DOW-OH ion-exchange resin column. Methyl methacrylate (17.72 g, 0.175 mol), cumyl dithiobenzoate (0.239 g, 8.80 mmol), azobisisobutyronitrile (AIBN) (0.0291g, 0.177 mmol), and dimethylformamide (18.01 g) were then combined in a Schlenk flask and subjected to four freeze-pump-thaw cycles. The flask was then placed in a 60°C bath for 8.8 hours. After thawing the solvent was removed on the vacuum line. The polymer was re-dissolved in tetrahydrofuran, precipitated in methanol, and dried until constant weight. Final Conversion: 62%. Molecular weight: 14,900 Da (GPC), 13,400 Da (theoretical). Dispersity index: 1.19.

### PTAMAUD-b-PPG-b-PTAMAUD

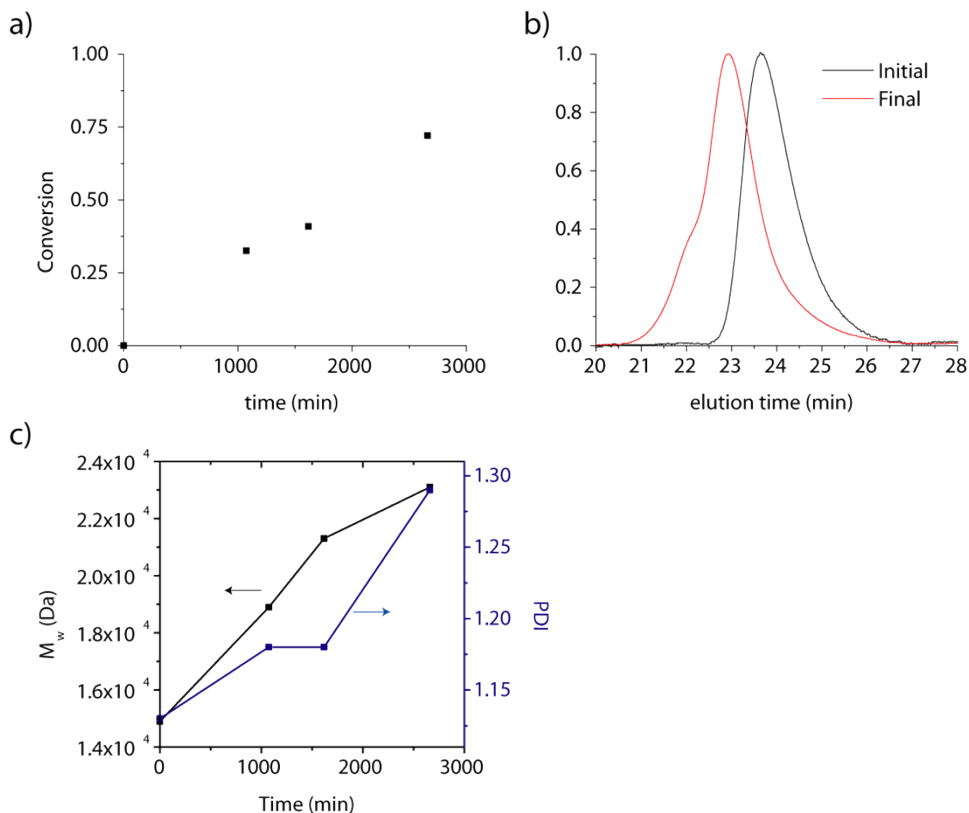
TAMAUD was de-inhibited by passing it in dichloromethane over a basic alumina/activated carbon column (~ 1:1 gram column to gram monomer). The monomer (5.53 g, 17.5 mmol), PPG)-CTA (1.51 g, 0.354 mmol), AIBN (0.0118g, 7.2×10<sup>-2</sup> mmol), and dimethylformamide (6.83 g) were then combined in a Schlenk flask and subjected to 4 freeze-pump-thaw cycles. The flask was then placed in a 60 °C bath for 18.8 hours. Afterwards the solvent was removed on the vacuum line. The resulting solution was precipitated from dichloromethane into methanol, and the polymer rich phase recovered by centrifugation. Final Conversion: 94%. *M<sub>n</sub>*: 23,100 Da (<sup>1</sup>H NMR), 17,900 Da (theoretical).



**Figure 1.** a) <sup>1</sup>H NMR of PPPG-*b*-PTAMAUD. b) GPC traces. [TAMAUD]<sub>0</sub>: [CTA]<sub>0</sub>: [AIBN]<sub>0</sub> = 200:1:0.2, 60 °C, 50% wt. DMF.

#### PMMA-*b*-PTAMAUD

TAMAUD was de-inhibited by passing it over a basic alumina/activated carbon column (~ 1:1 gram column to gram monomer). The monomer (5.00 g, 15.9 mmol), PMMA-CTA (3.40 g, 0.228 mmol), AIBN (0.0055g, 3.3×10<sup>-2</sup> mmol), and dimethylformamide (7.94 g) were then combined in a Schlenk flask and subjected to four freeze-pump-thaw cycles. The flask was then placed in a 60 °C bath for 44.4 hours. Afterwards the solvent was removed on the vacuum line. The polymer was then purified by precipitation in methanol and water. Final conversion: 72%. Molecular weight: 21,200 Da (<sup>1</sup>H NMR), 26,200 Da (theoretical).



**Figure 2.** Plots of a) Conversion versus time, b) GPC traces, and c) molecular weight evolution (PMMA standard) for PMMA-*b*-PTAMAUD. [TAMAUD]<sub>0</sub>: [CTA]<sub>0</sub>: [AIBN]<sub>0</sub> = 200:1:0.1, 60 °C 50% wt. DMF.

#### PMMA-*b*-PIL

In general, PMMA-*b*-PTAMAUD, IL (1.1 molar equivalents to thioacetate groups), and 2 volume equivalents of 50/50 DCM and methanol were combined. The mixture was then sonicated to dissolve the polymer, and DBU was added (0.1 molar equivalents

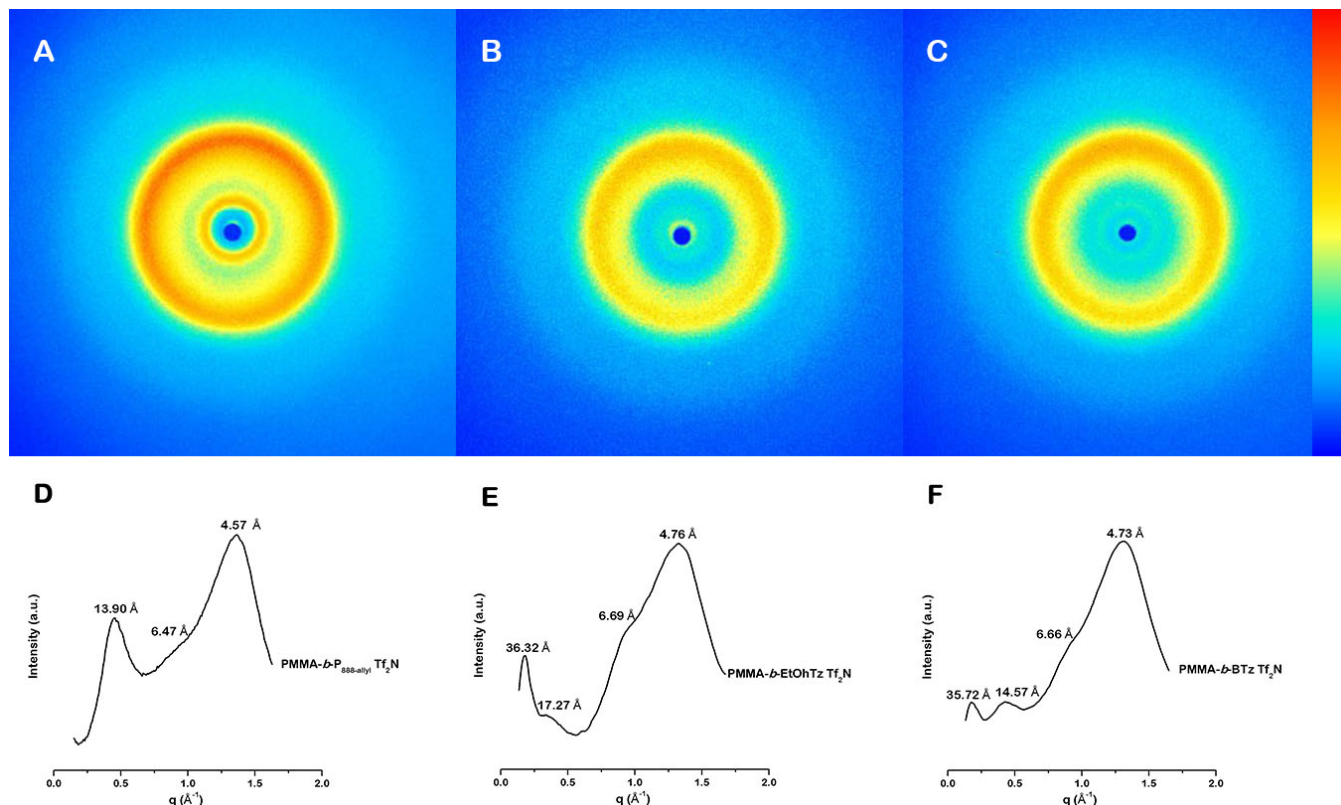
to thioacetate groups). After stirring for 4 hours at room temperature the mixture was precipitated into a 50/50 mixture of water and methanol.

PMMA-*b*-PIL films were casted using DCM as a solvent cast onto Rain-ex™ coated glass. The films were used without any further treatment.

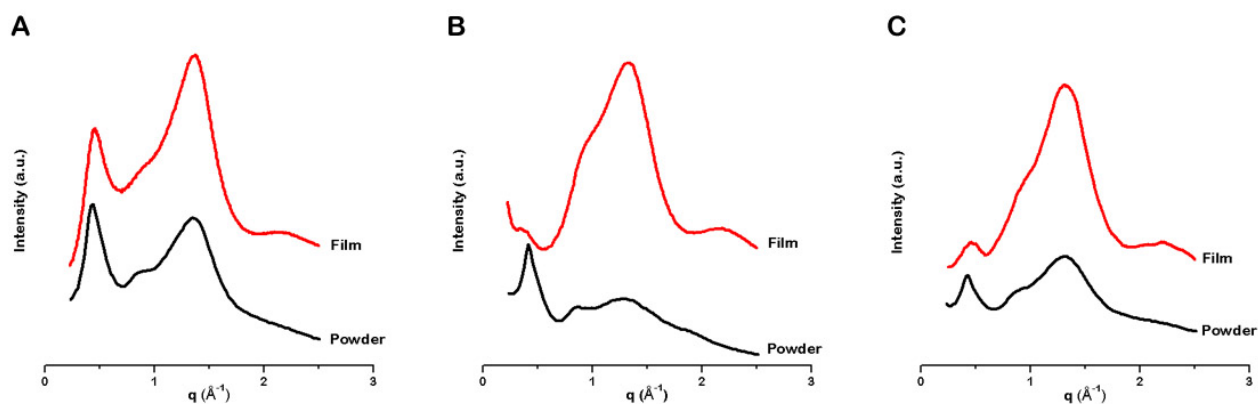
#### Crosslinked *p*(PG-*b*-TAMAUD) films

A mixture of PPG-*b*-PTAMAUD, IL and oligoethyleneoxide diacrylate was prepared and diluted in 0.25 to 2.0 volume equivalents of 2:2 to 9:1 DCM and methanol. A ratio of thioacetate to olefin of 1.1 was used, and ratios of IL to di-acrylate of 4:1 were employed. DBU was then added (0.1 molar equivalents to thioacetate groups) and the mixtures cast onto Rain-ex™ coated glass.

#### Small and Wide Angle X-Ray Scattering



**Figure 3.** WAXS of a) PMMA-*b*-P<sub>888-allyl</sub>Tf<sub>2</sub>N, b) PMMA-*b*-EtOhTz Tf<sub>2</sub>N, and c) PMMA-*b*-BTz Tf<sub>2</sub>N. 2-D representation of scattering intensity vs. scattering vector shown in figures d-f.  $d$ -spacing values are labeled.



**Figure 4.** WAXS profiles of powder and film samples for a) PMMA-*b*-P<sub>888-allyl</sub>Tf<sub>2</sub>N, b) PMMA-*b*-EtOhTz Tf<sub>2</sub>N, and c) PMMA-*b*-BTz Tf<sub>2</sub>N.

Measurement of gas separation performance:

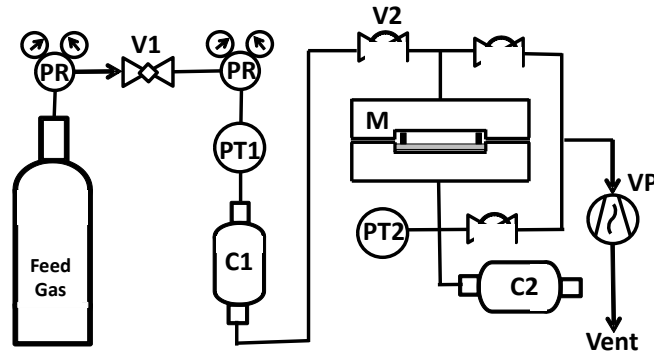


Figure 1: Isochoric permeation system for measuring gas separation performance of membranes. (C1) Feed Ballast Volume, (C2) Permeate Ballast Volume, (PT1) Upstream Pressure Transducer, (PT2) Downstream Pressure Transducer, (PR) Pressure Regulators, (V1) Plug Valve, (V2) Diaphragm Valve, (VP) Vacuum Pump, and (M) Membrane Holder.

The membrane was loaded in the Millipore high pressure stainless 25 mm filter holder. The entire permeation system was degassed using a vacuum pump (Edwards nXDS 10i scroll pump) for 18 hours and then the leak rate was measured before each permeation experiment by isolating the permeation system from the vacuum pump to obtain the accurate permeability measurements. The leak rate was much less than (at least 10 times) the steady state pressure rise of the gas permeation measurement. The feed gas is then introduced to the upstream side of the membrane, and the pressure rise in the downstream volume was recorded as a function of time. A typical plot of pressure change as a function of time obtained from permeation measurement is shown in Figure 2.

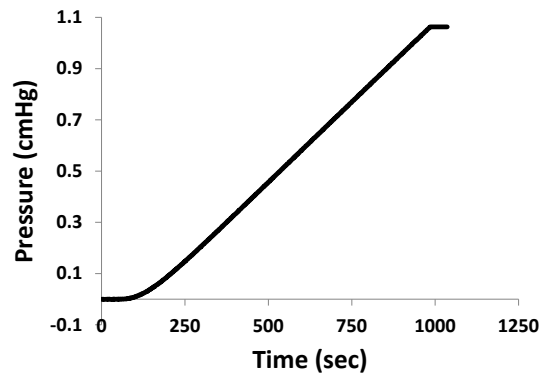


Figure 2: Typical plot of downstream steady state pressure rise with time.

Permeability is calculated by taking a differentiation of pressure rise as a function of time and using the following equation:

$$P_A = \frac{V_d \cdot l}{p_2 \cdot A \cdot R \cdot T} \left[ \left( \frac{dp_1}{dt} \right)_{ss} - \left( \frac{dp_1}{dt} \right)_{leak} \right]$$

Where,  $V_d$ = downstream volume ( $\text{cm}^3$ ),  $l$  = film thickness (cm),  $p_2$  = upstream absolute pressure (cmHg),  $A$  = film area ( $\text{cm}^2$ ),  $T$  = Temperature (K),  $R$ = gas constant ( $\text{cm}^3 \text{cmHg/mol} \cdot \text{K}$ ),  $(dp_1/dt)_{ss}$  = rate of pressure rise under upstream pressure (cmHg/sec),  $(dp_1/dt)_{leak}$  = rate of pressure rise under vacuum (cmHg/sec).