

Supporting information

**Ring-opening polymerization-induced self-assembly (ROPISA) of salicylic acid *o*-carboxyanhydride**

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## General Methods.

Triphosgene, activated carbon, anhydrous dichloromethane (DCM) and 2-tert-butylimino-2-diethylamino-1,3-dimethylperhydro-1,3,2-diazaphosphorine (BEMP) were purchased from INNOCHEM and used without treatment. Salicylic acid (SA), 3,5-bis(trifluoromethyl) phenyl isocyanate, aniline and triethylamine (TEA) were purchased from J&K SCIENTIFIC LTD and used without treatment. Tetrahydrofuran (THF) and ethyl ether (EE) were distilled over sodium/benzophenone and stored over 4Å molecular sieves prior to use. Methyloxypolyethylene glycol ( $M_n = 2000$ , MPEG-OH) purchased from INNOCHEM was azeotroped with toluene to remove water.  $\text{CDCl}_3$  was purchased from Cambridge Isotope Laboratories. All the polymerization reactions were performed in a Vigor glove box.

## Characterization.

The  $^1\text{H}$  NMR analysis were carried out on a 400 MHz or 500 MHz NMR instrument (Bruker Corporation, Germany) at room temperature using  $\text{CDCl}_3$  ( $\delta = 7.26$  ppm for  $^1\text{H}$  NMR, 77.16 ppm for  $^{13}\text{C}$  NMR) as solvent. GPC measurements were carried out by Agilent LC 1260 instrument equipped with a differential refractive-index detector. One guard column and two 7.5 x 300 mm PLgel MIXED-C columns were used. The measurements were performed using DMF as eluent (flow rate of 1.0 mL/min at 55 °C, 0.04 M LiBr), and polymethyl methacrylate were employed for calibration.

*In situ* IR study was carried out by using ReactIR 15<sup>m</sup> with MCT Detector from METTLER TOLEDO AutoChem. DiComp (Diamond) probe was connected via AgX 6 mm x 2 m Fiber (Silver Halide). Spectra were taken from 2000  $\text{cm}^{-1}$  to 650  $\text{cm}^{-1}$  at 8 wavenumber resolution and the automatic sampling interval was 15 second. In the process of polymerization, the sample was taken from the polymerization system at the determined time, and spotted on the KBr plate for scanning on FT-IR (Nicolet 6700, the accumulation rate was 16 times with 4 wavenumber resolution). The monomer conversion was determined by the intensity ratio between 1738  $\text{cm}^{-1}$  and 1754  $\text{cm}^{-1}$ , conversion% =  $I_{1738} / (I_{1738} + I_{1754})$ .<sup>[1]</sup>

The morphology of the nanoparticles in THF (8.0  $\mu\text{L}$ , 1.0 mg/mL) were dropped onto a copper grid and dried at ambient temperature without staining. Images were recorded on a Hitachi HT7700 transmission electron microscope operated with 100 KV.

Dynamic light scattering (DLS) analysis was carried out using a commercial laser light scattering spectrometer (ZEN3600, Malvern) with Zetasizer software. All data were averaged over three measurements and the nanoparticle concentrations were diluted to 1.0 mg/mL.

### **Synthesis of SAOCA monomer.**

To a solution of triphosgene (15 mmol) and activated charcoal (~90 mg) in anhydrous diethyl ether (40 mL), salicylic acid (36.0 mmol) was stepwise added. The reaction mixture was stirred for 3 hours at -20°C. Subsequently, a solution of triethylamine (4 mL, 28 mmol) in diethyl ether solution (20 mL) was gradually participated. The reaction mixture was stirred for 3 hours at room temperature, and the mixture was filtered over MgSO<sub>4</sub>. The filtrate was concentrated and the resulting residue was recrystallized from THF/ether/hexane (v/v/v = 5/15/3) twice to give white crystal in a yield of 35%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>), δ (ppm): 8.10 (*d*, *J* = 7.8 Hz, 1H, *ArH*), 7.84 (*t*, *J* = 7.9 Hz, 1H, *ArH*), 7.46 (*t*, *J* = 7.6 Hz, 1H, *ArH*), 7.34 (*d*, *J* = 8.4 Hz, 1H, *ArH*). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz), δ (ppm): 155.71 (C=O), 153.81 (*ArC*), 142.15 (OC=OO), 138.67 (*ArC*), 130.08 (*ArC*), 126.78 (*ArC*), 116.82 (*ArC*), 109.83 (*ArC*).

### **Preparation of 3,5-bis (trifluoromethyl)-phenyl -3- phenylurea (U-1)**

As reported<sup>[2]</sup>, U-1 was synthesized by the modified procedure. Under nitrogen atmosphere, aniline (3.91 mol) was added to a solution of 3,5-bis (trifluoromethyl) phenyl isocyanate (3.91 mmol) in anhydrous DCM. After stirring at room temperature overnight, the solvent was removed in vacuum to yield 93%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>), δ (ppm): 7.89 (*s*, 1H, -NH-*ArH*-C(CF<sub>3</sub>)-), 7.54 (*s*, 1H, -NH-*ArH*-C(CF<sub>3</sub>)-*ArH*), 7.41 (*t*, *J* = 5.6 Hz, 1H, *ArH*), 7.39 – 7.34 (*m*, 1H, *ArH*), 7.24 (*d*, *J* = 7.5 Hz, *ArH*), 6.85 (*s*, 1H, -NH-*Ar*), 6.55 (*s*, 1H, O=NH-C<sub>6</sub>H<sub>5</sub>).

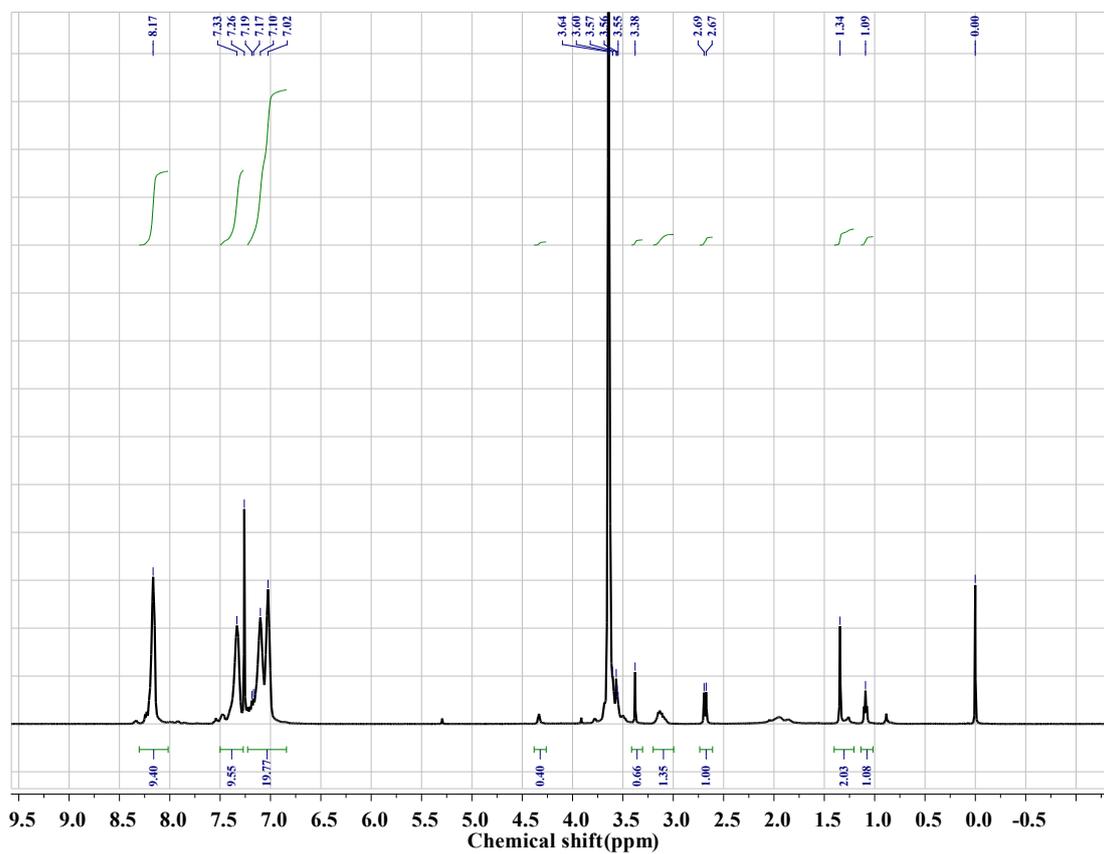
### **Polymerization procedure.**

A typical procedure for polymerization of SAOCA was performed in a 25 mL Schlenk in a Vigor glovebox. The determined amount of BEMP, U-1 and MPEG-OH was stirred in 1.0 mL THF for 10 min, followed by the addition of SAOCA (0.75 mmol). At a specific time, a small aliquot of polymer solution was taken out for measuring monomer conversion. The final reaction solution was precipitated in the mixture of ethyl acetate/hexane (v/v = 1/1), and washed twice using the same solution. The obtained polymers were dried under vacuum for structural characterization.

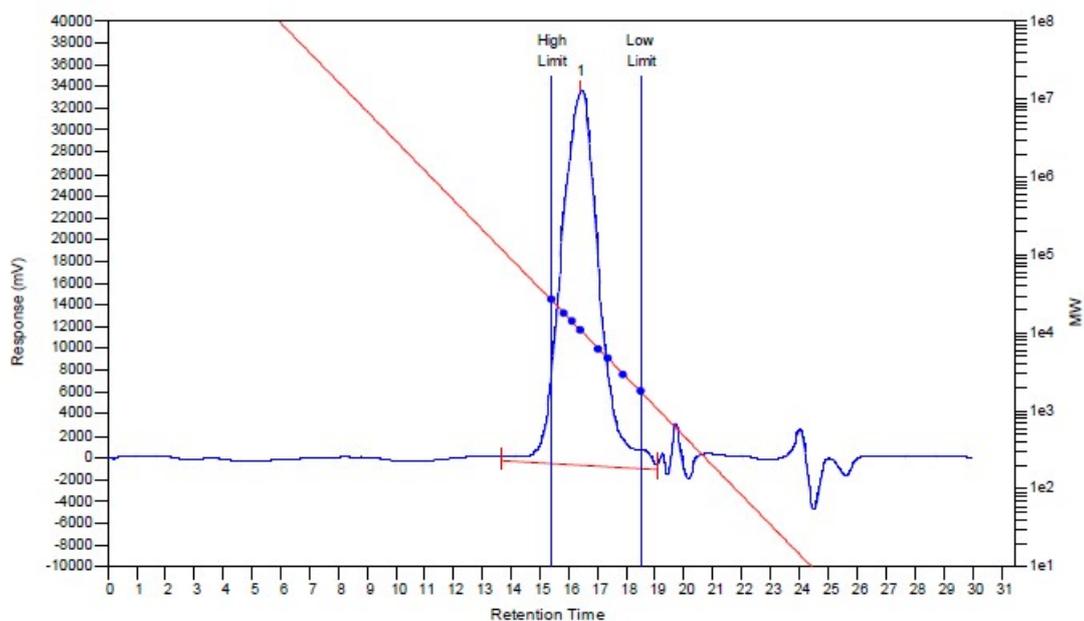
## References.

[1] Quan, Y. F. and Rong, T. *J. Am. Chem. Soc.*, **2017**, *139*, 6177.

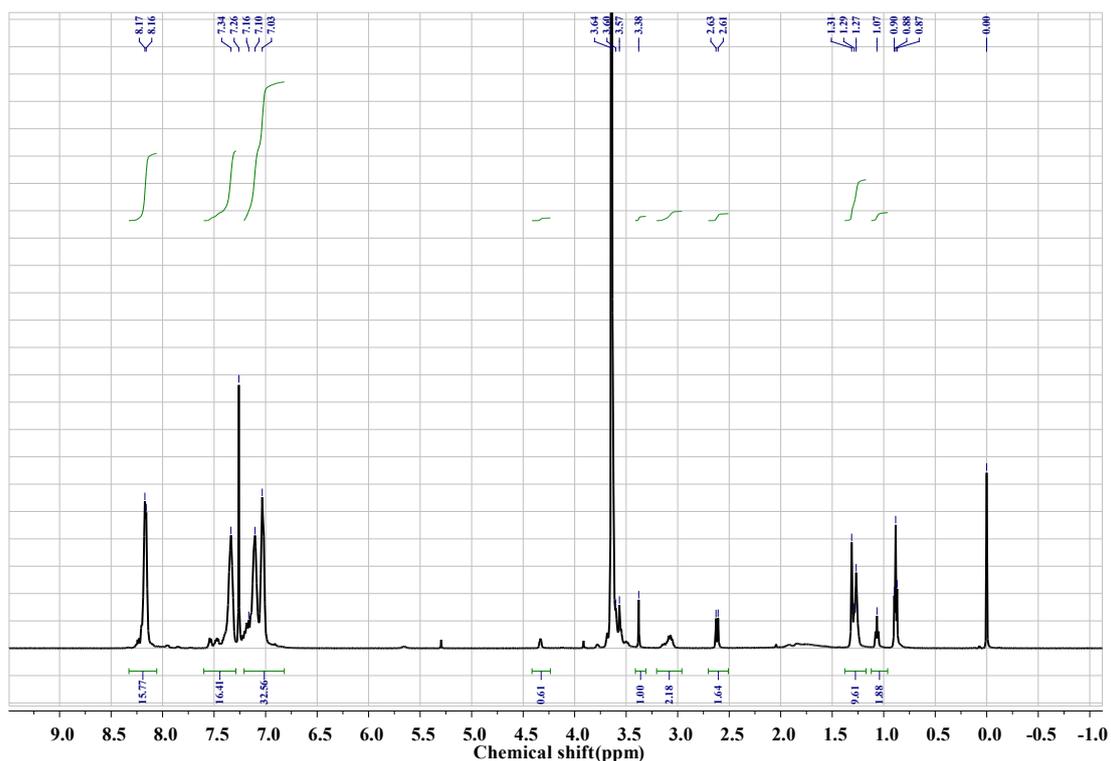
[2] Jiang, Z. L., Zhao, J. P. and Zhang, G. Z. *Chin. J. Polym. Sci.*, **2019**, *37(12)*, 1205-1223.



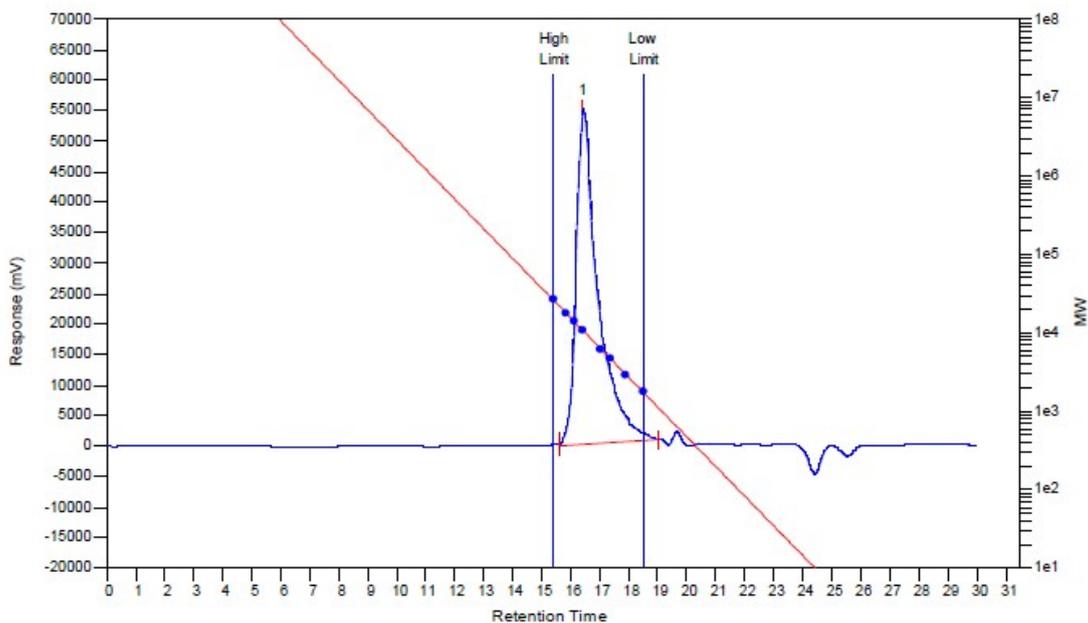
**Figure S1.** <sup>1</sup>H NMR spectrum of the polymer afforded at the feeding ratio of BEMP, MPEG-OH and SAOCA to 1/1/50 (Table 1, Entry 1).



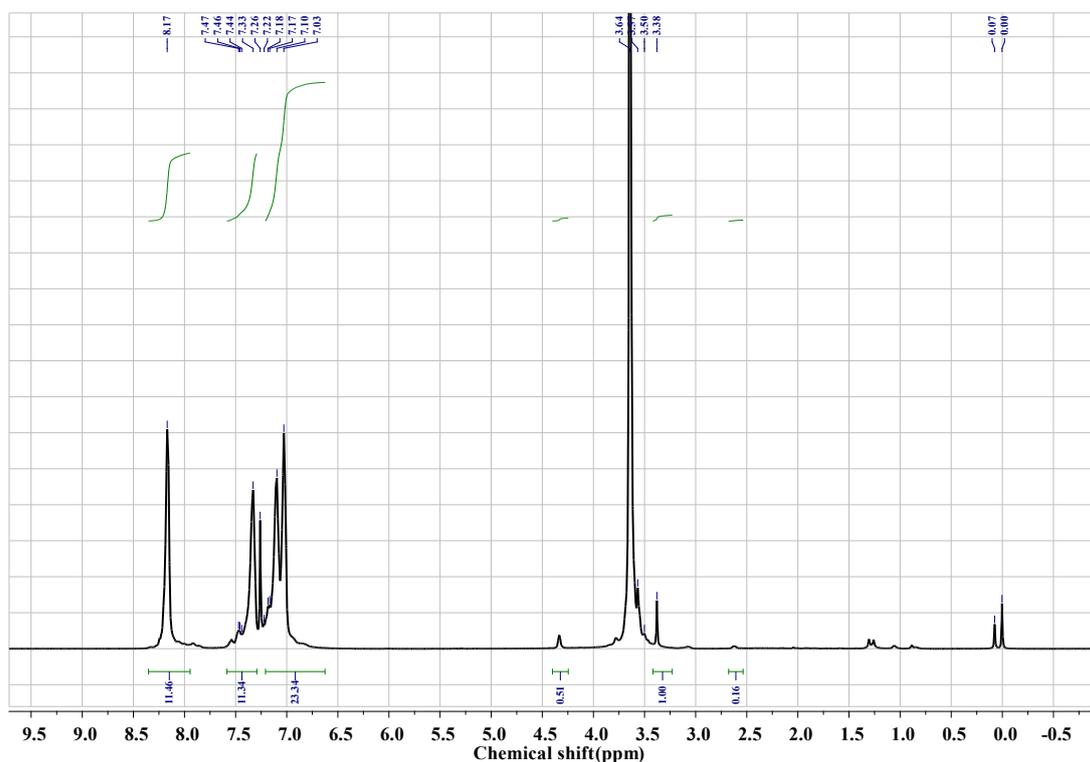
**Figure S2.** GPC trace of the polymer afforded at the feeding ratio of BEMP, MPEG-OH and SAOCA to 1/1/50 (Table 1, Entry 1).



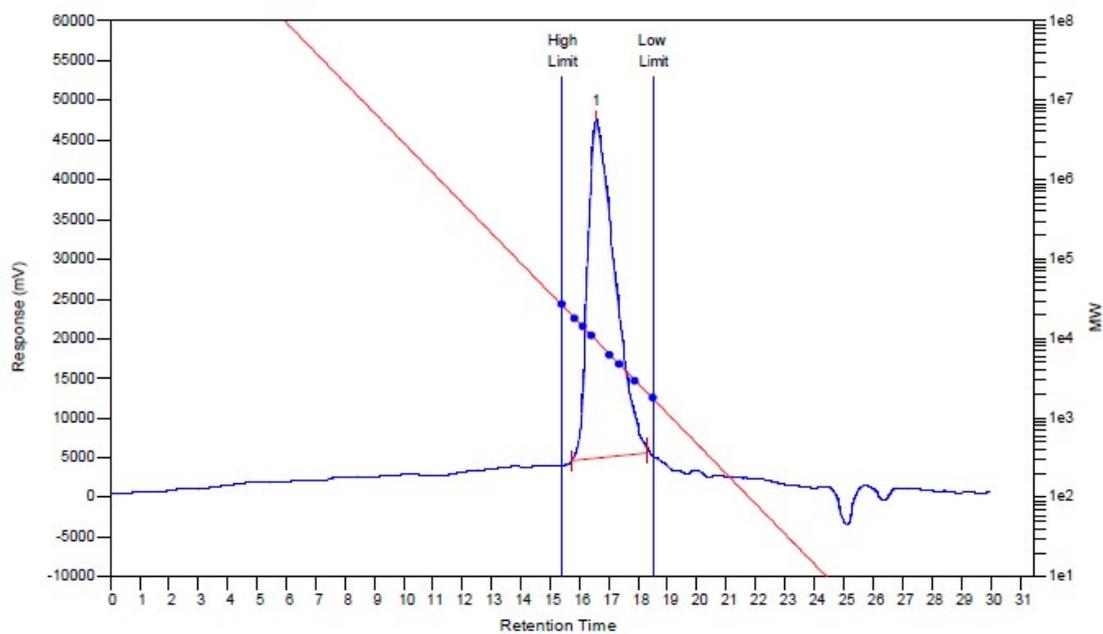
**Figure S3.** <sup>1</sup>H NMR spectrum of the polymer afforded at the feeding ratio of BEMP, U-1, MPEG-OH and SAOCA to 1/1/1/50 (Table 1, Entry 2).



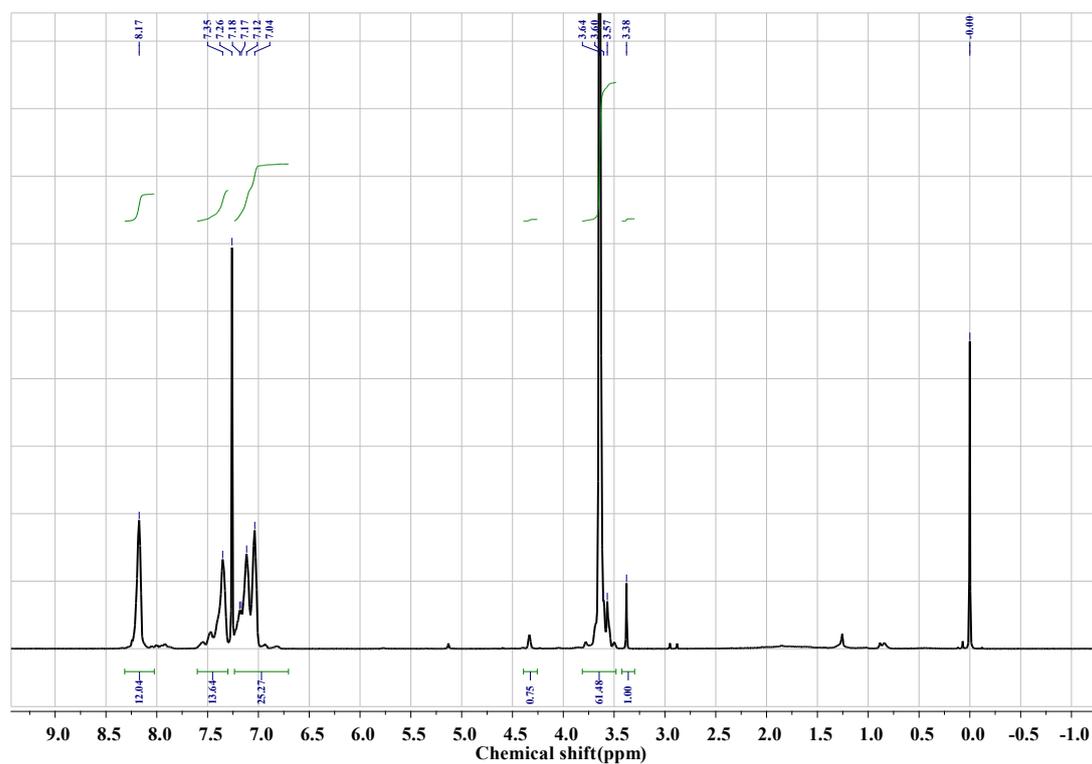
**Figure S4.** GPC trace of the resulting polymers via ROP of SAOCA using [BEMP]:[MPEG-OH]:[U-1]:[SAOCA] = 1:1:1:50 (Table 1, Entry 2).



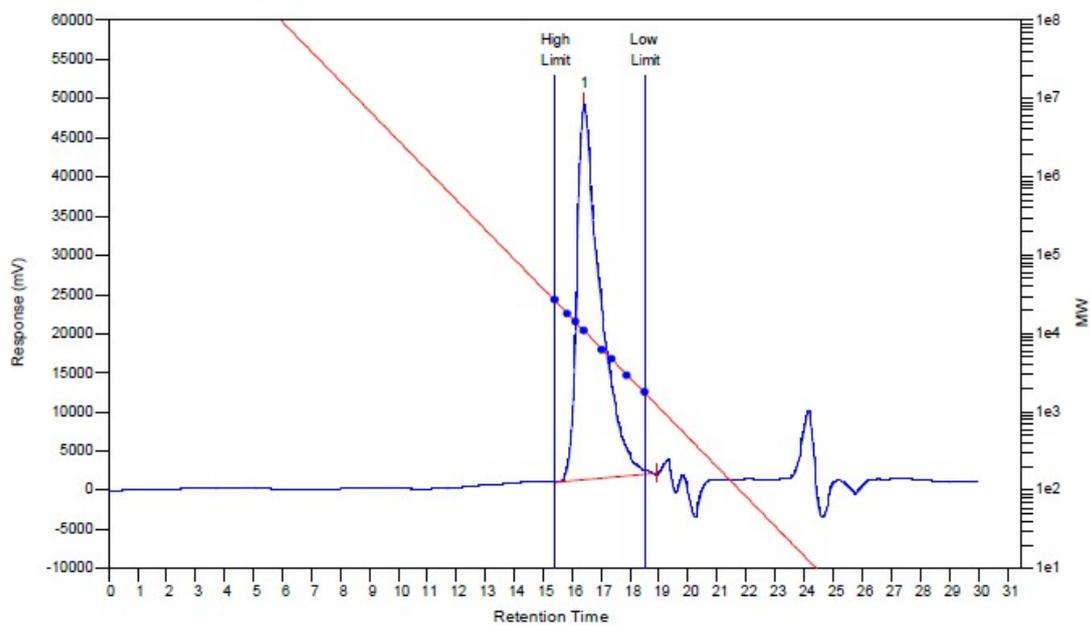
**Figure S5.**  $^1\text{H}$  NMR spectrum of the polymer afforded at the feeding ratio of BEMP, U-1, MPEG-OH and SAOCA to 0.5/1/1/50 (Table 1, Entry 3).



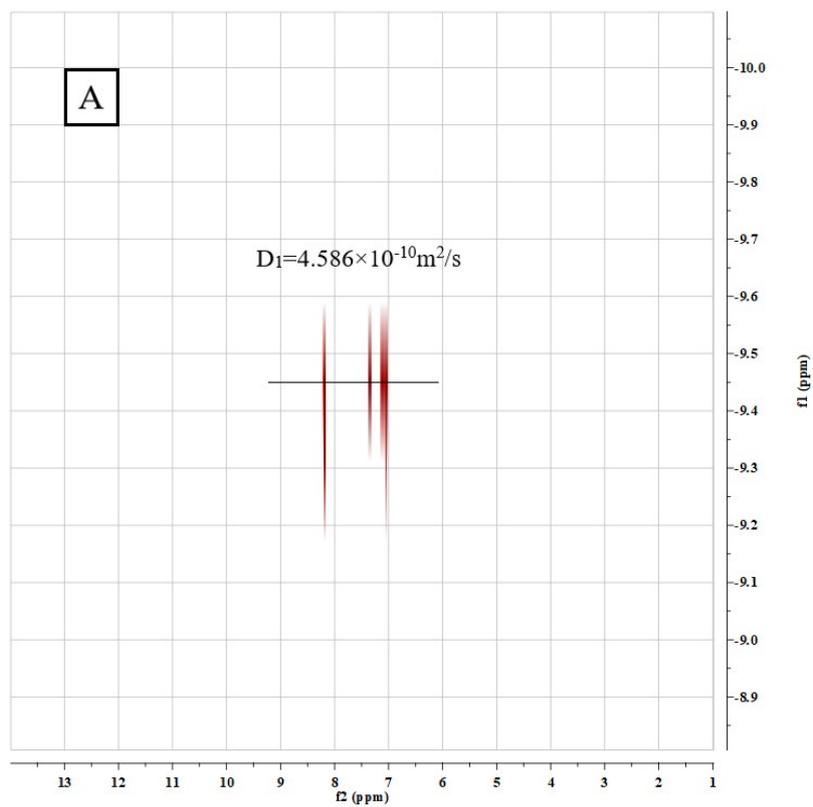
**Figure S6.** GPC curve of the resulting polymers via ROP of SAOCA using [BEMP]:[MPEG-OH]:[U-1]:[SAOCA] = 0.5:1:1:50 (Table 1, Entry 3).

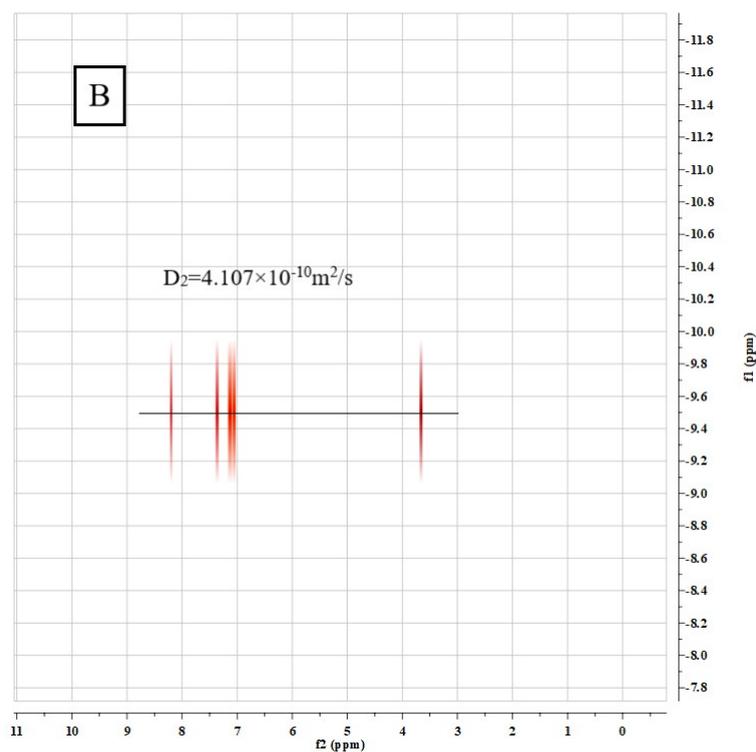


**Figure S7.**  $^1\text{H}$  NMR spectrum of the polymer afforded at the feeding ratio of BEMP, U-1, MPEG-OH and SAOCA to 0.25/1/1/50 (Table 1, Entry 4).

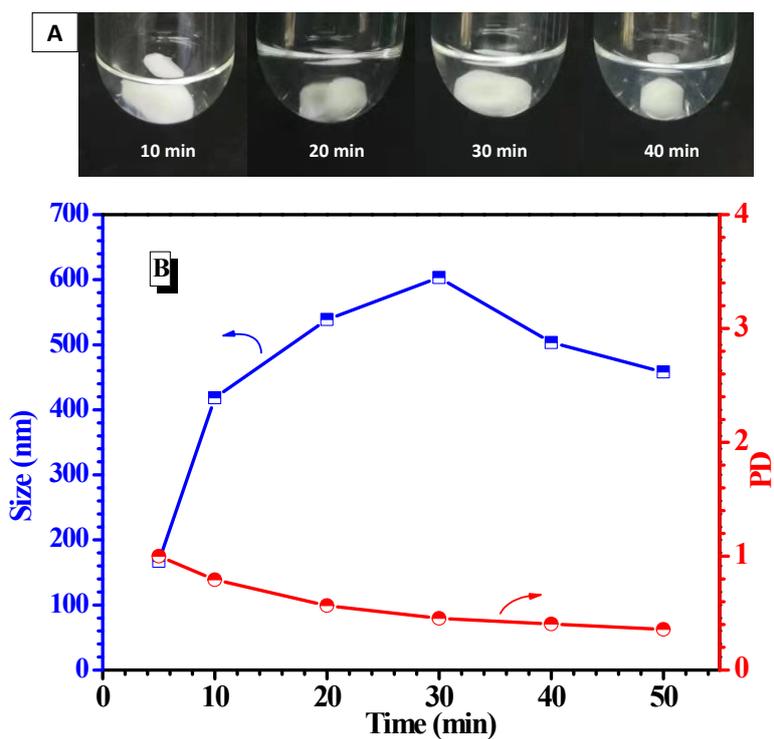


**Figure S8.** GPC curve of the resulting polymers via ROP of SAOCA using [BEMP]:[MPEG-OH]:[U-1]:[SAOCA] = 0.25:1:1:50 (Table 1, Entry 4).

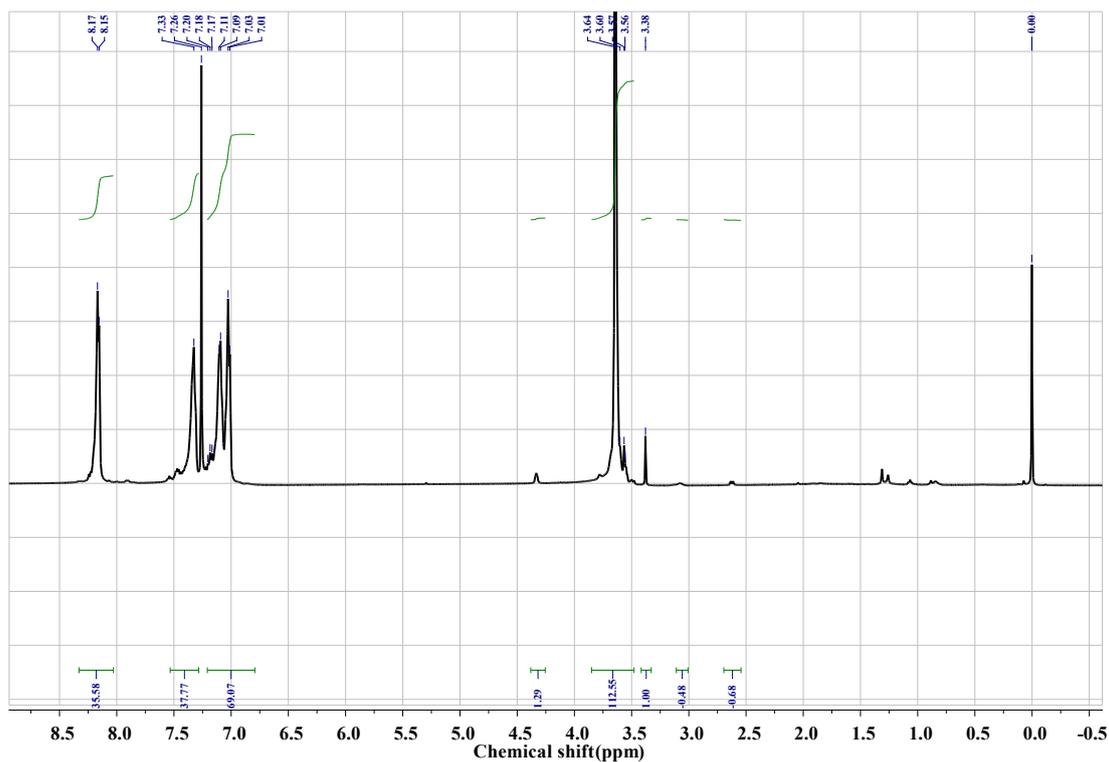




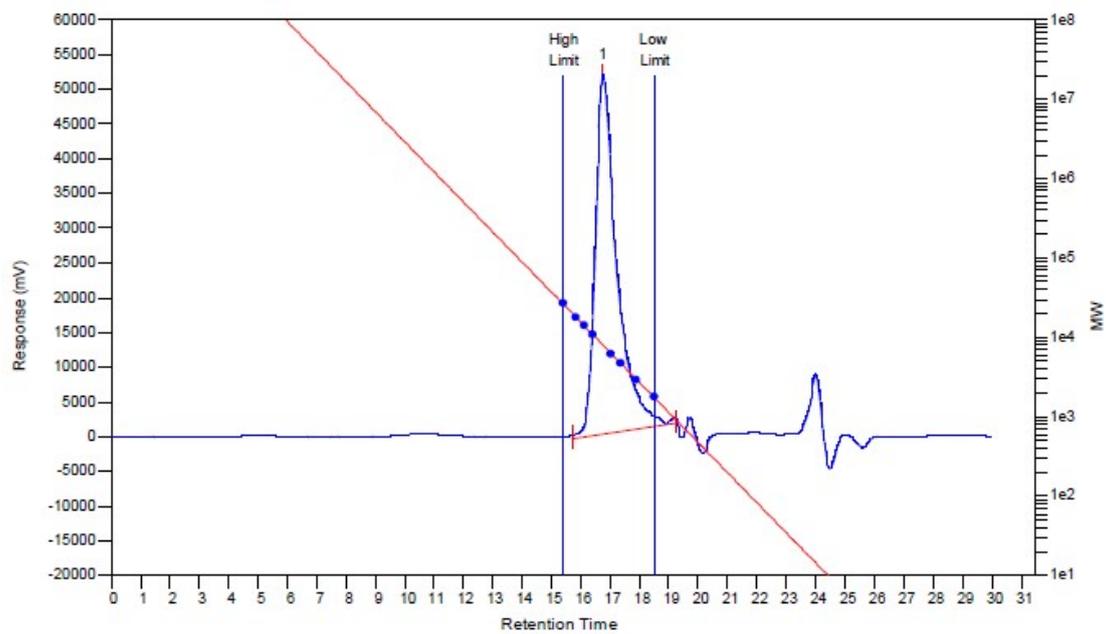
**Figure S9.** DOSY spectra of (A) homopolymer PSA and (B) block copolymer MPEG-*b*-PSA.



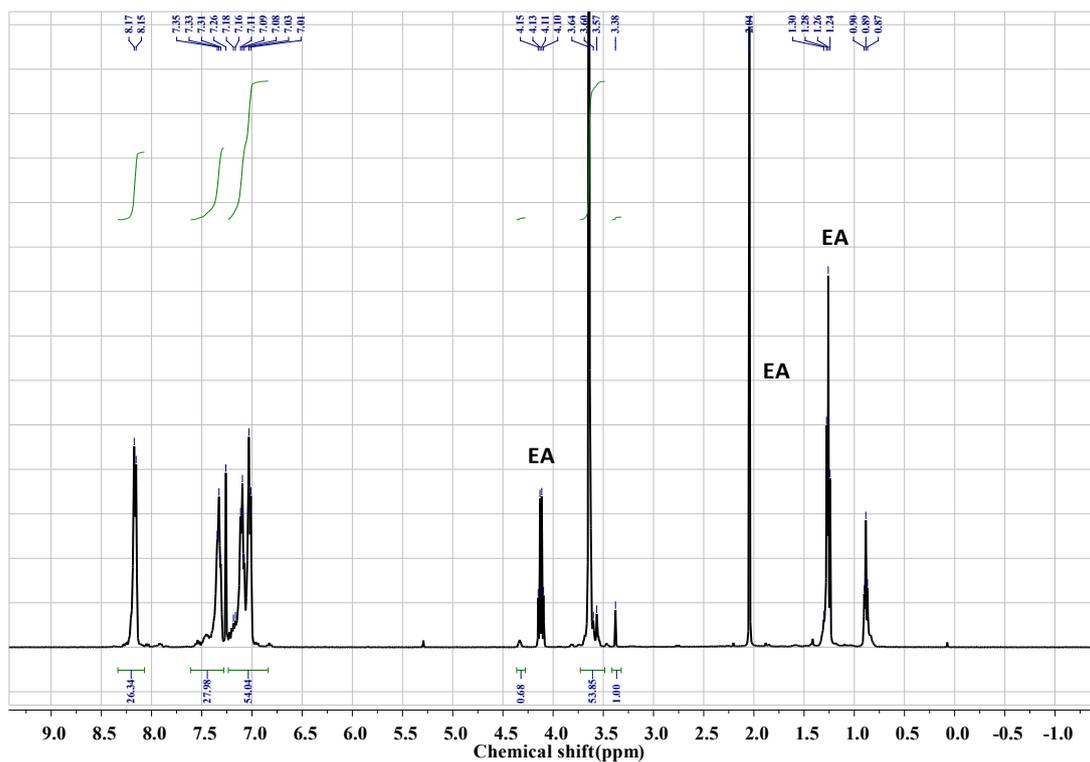
**Figure S10.** (A) Images of polymerization solution in the process of ROPISA; (B) Diameter and polydispersity change in the process of polymerization carried by the feeding ratio of BEMP, U-1, MPEG-OH and SAOCA to 0.25/1/1/50 in THF at 25 °C, [SAOCA] = 0.75 M.



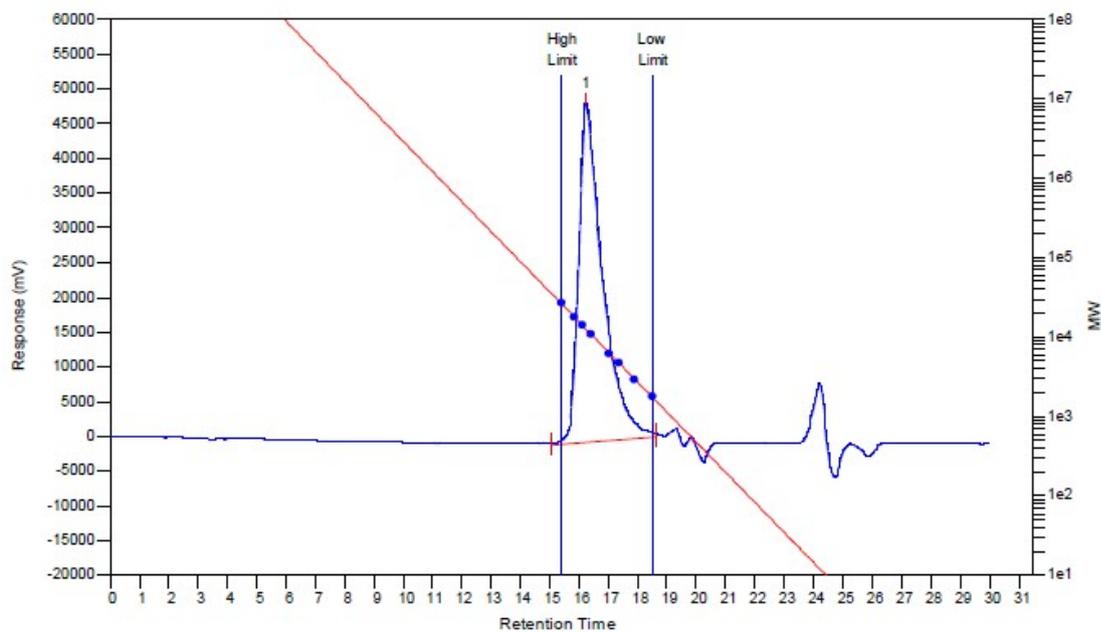
**Figure S11.**  $^1\text{H}$  NMR spectrum of the polymer afforded at the feeding ratio of BEMP, U-1, MPEG-OH and SAOCA to 0.25/1/1/25 (Table 1, Entry 5).



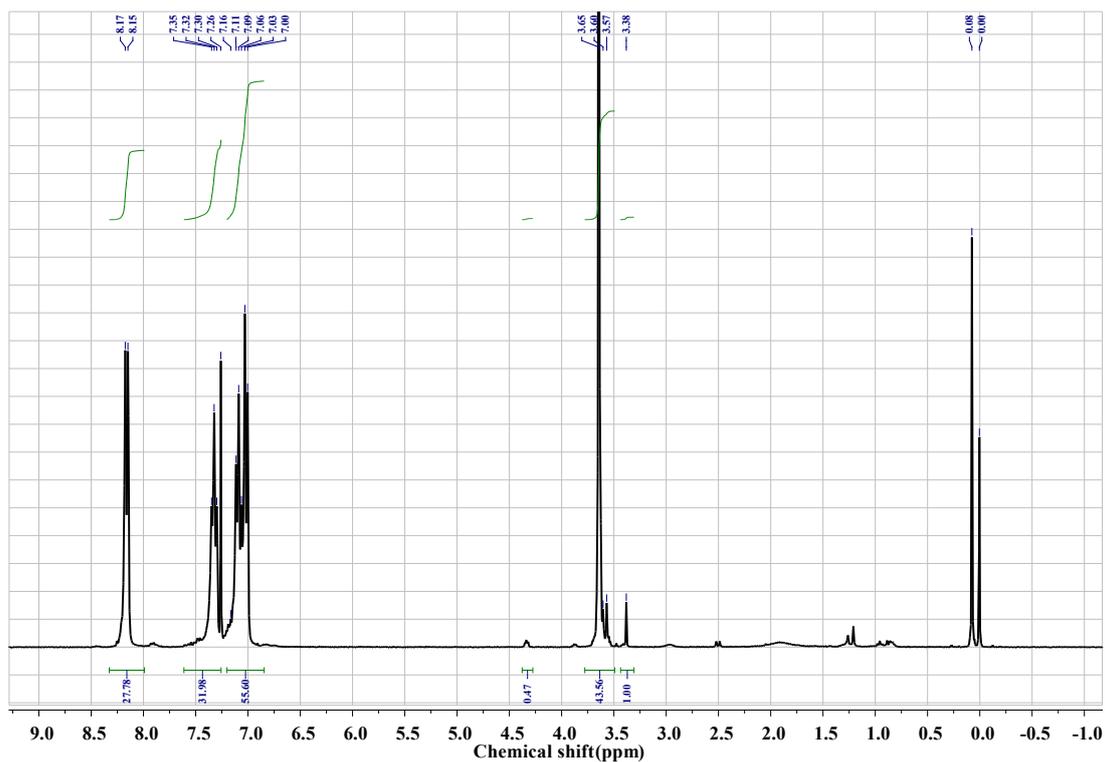
**Figure S12.** GPC curve of the resulting polymers via ROP of SAOCA using [BEMP]:[U-1]: [MPEG-OH]:[SAOCA] = 0.25/1/1/25 (Table 1, Entry 5).



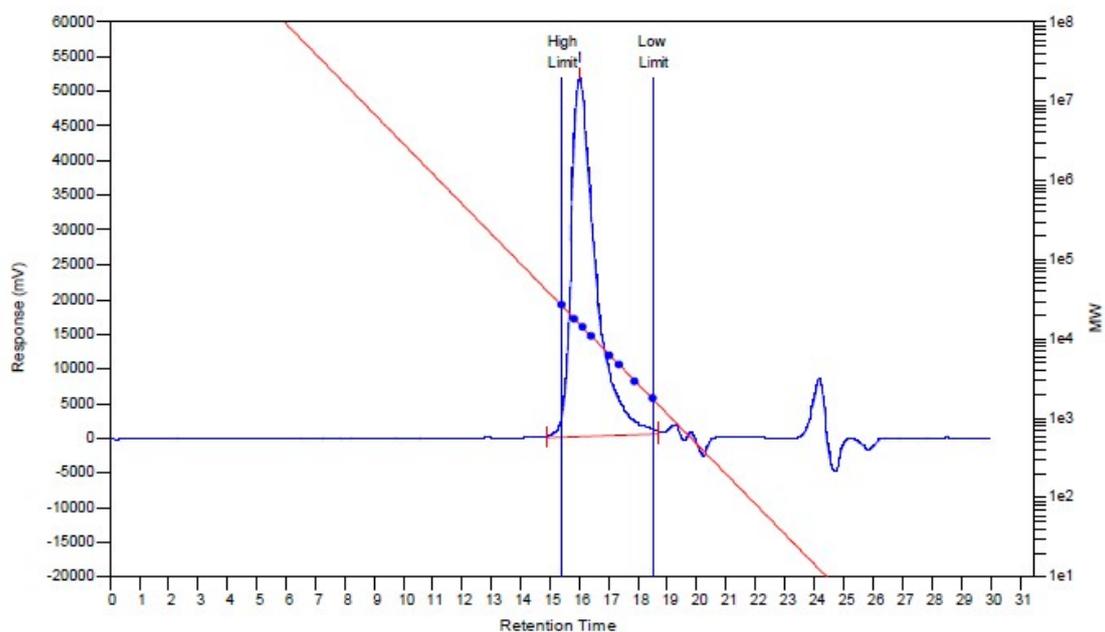
**Figure S13.**  $^1\text{H}$  NMR spectrum of the polymer afforded at the feeding ratio of BEMP, U-1, MPEG-OH and SAOCA to 0.25/1/1/75 (Table 1, Entry 6).



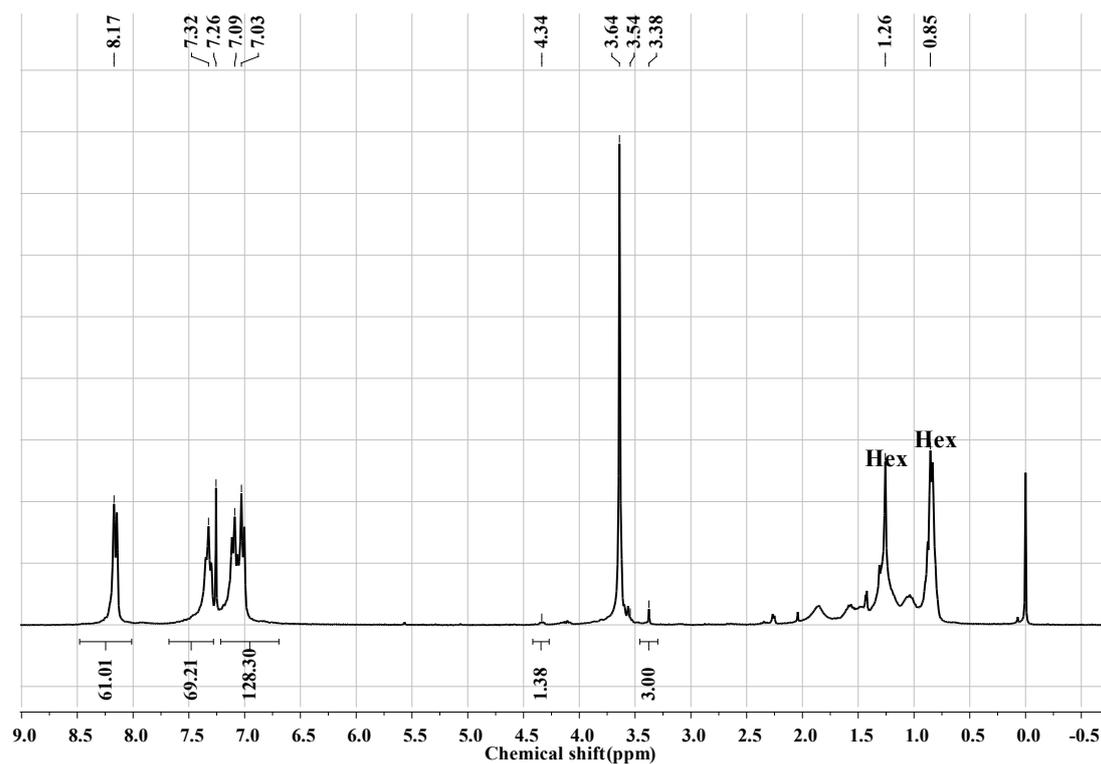
**Figure S14.** GPC curve of the resulting polymers via ROP of SAOCA using [BEMP]:[U-1]: [MPEG-OH]:[SAOCA] = 0.25:1:1:75 (Table 1, Entry 6).



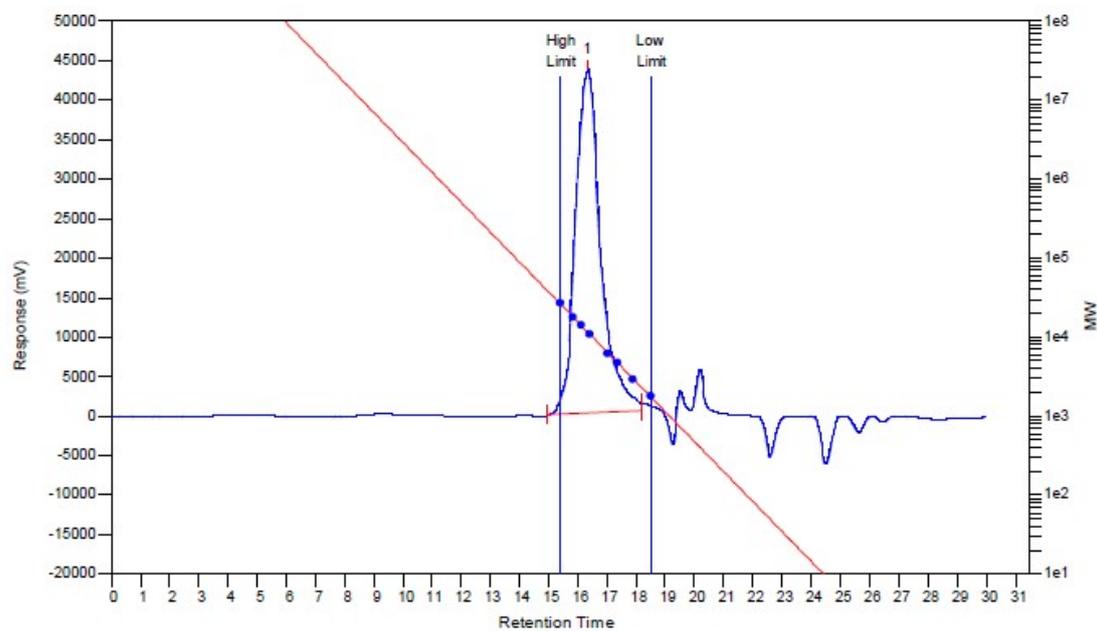
**Figure S15.**  $^1\text{H}$  NMR spectrum of the polymer afforded at the feeding ratio of BEMP, U-1, MPEG-OH and SAOCA to 0.25/1/1/100 (Table 1, Entry 7).



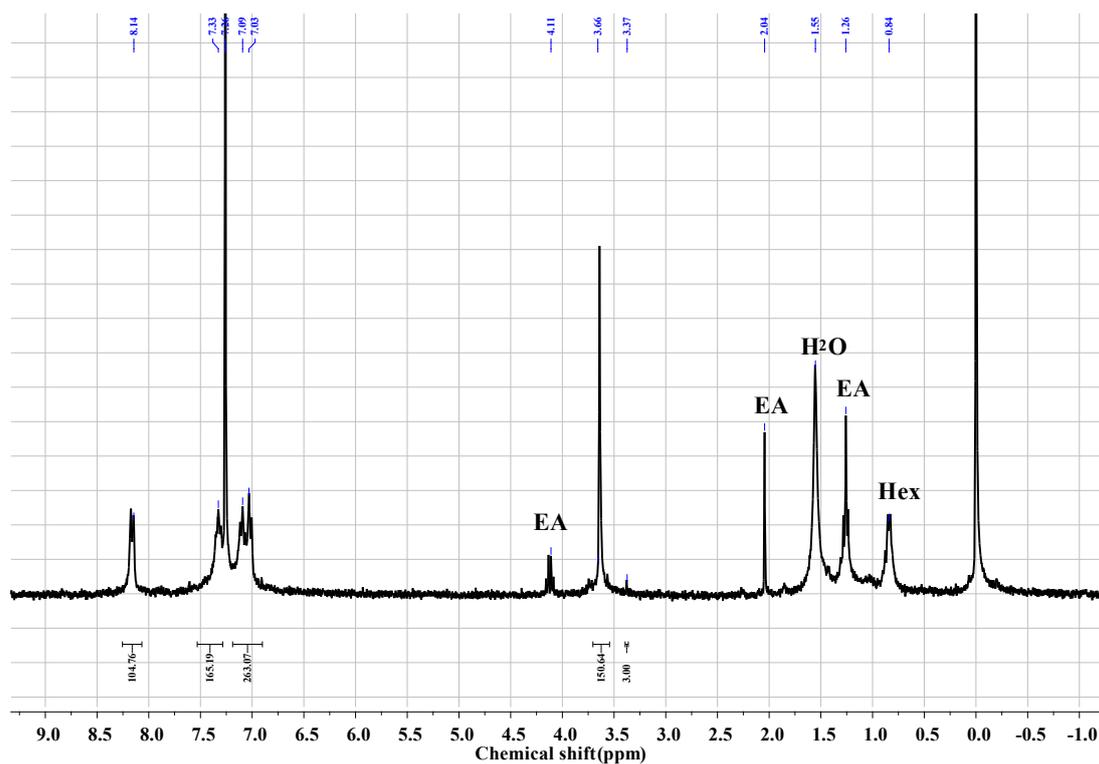
**Figure S16.** GPC curve of the resulting polymers via ROP of SAOCA using [BEMP]:[MPEG-OH]:[U-1]:[SAOCA] = 0.25:1:1:100 (Table 1, Entry 7).



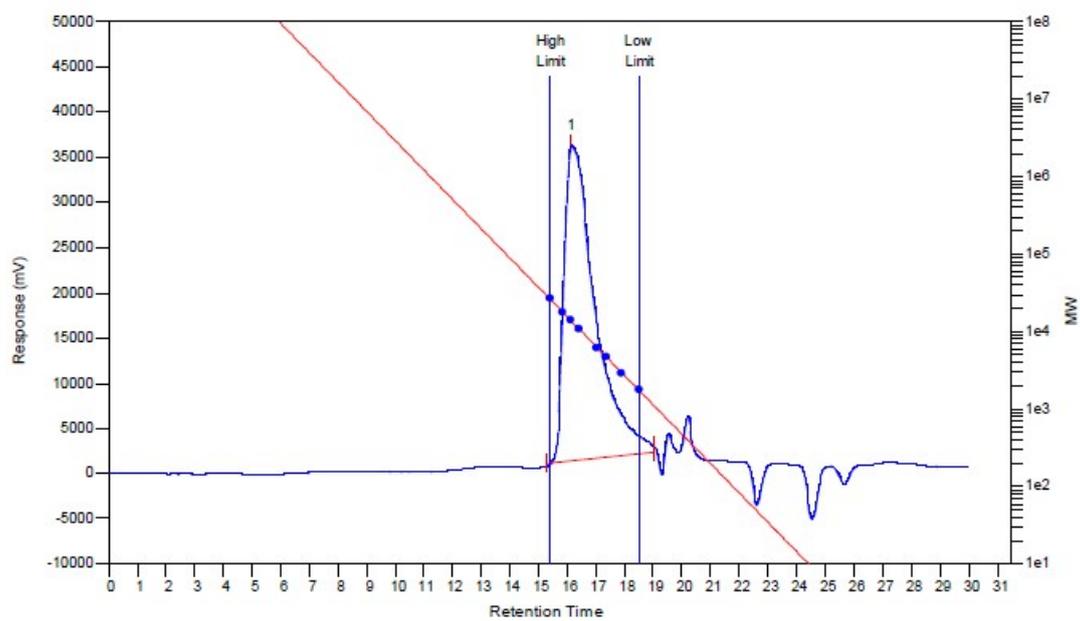
**Figure S17.**  $^1\text{H}$  NMR spectrum of the polymer afforded at the feeding ratio of BEMP, U-1, MPEG-OH and SAOCA to 0.25/1/1/125 (Table 1, Entry 8).



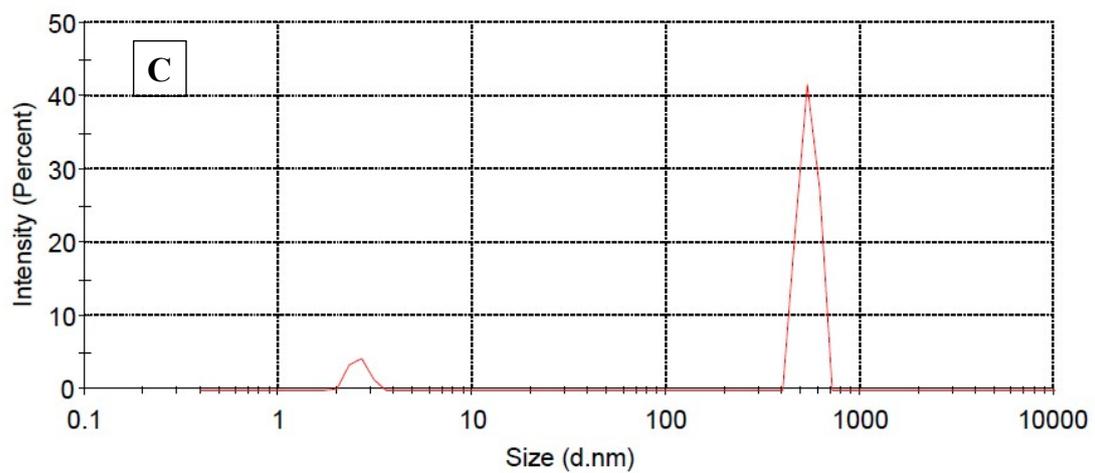
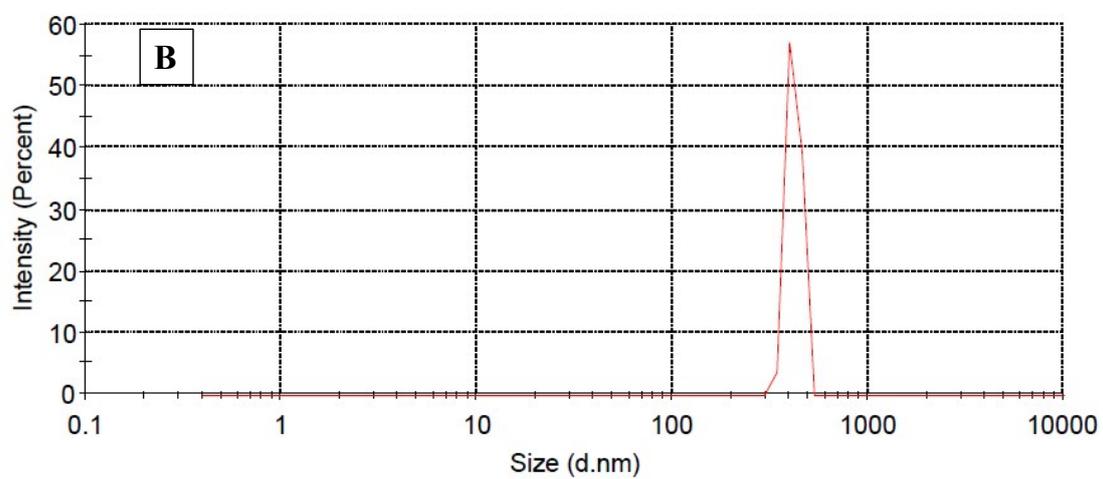
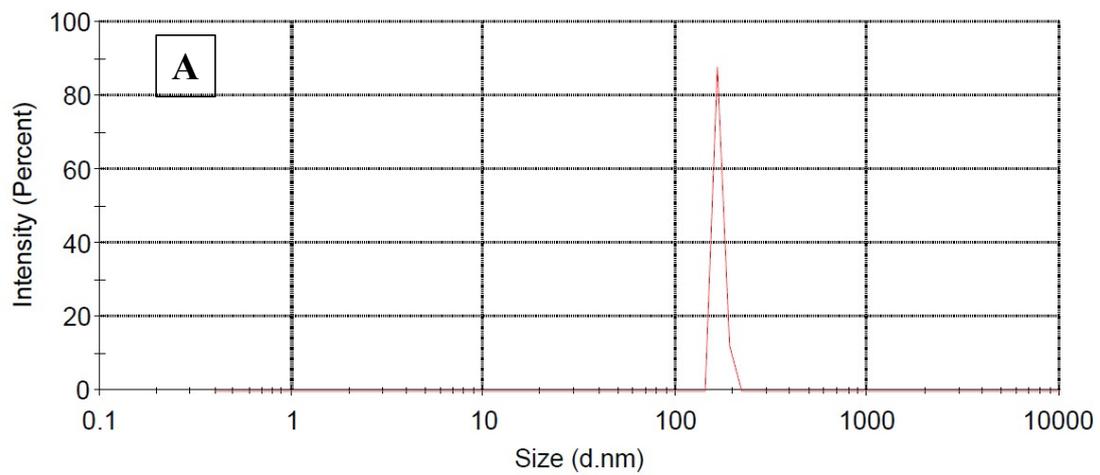
**Figure S18.** GPC trace of the resulting polymers via ROP of SAOCA using [BEMP]:[MPEG-OH]:[U-1]:[SAOCA] = 0.25:1:1:125 (Table 1, Entry 8).

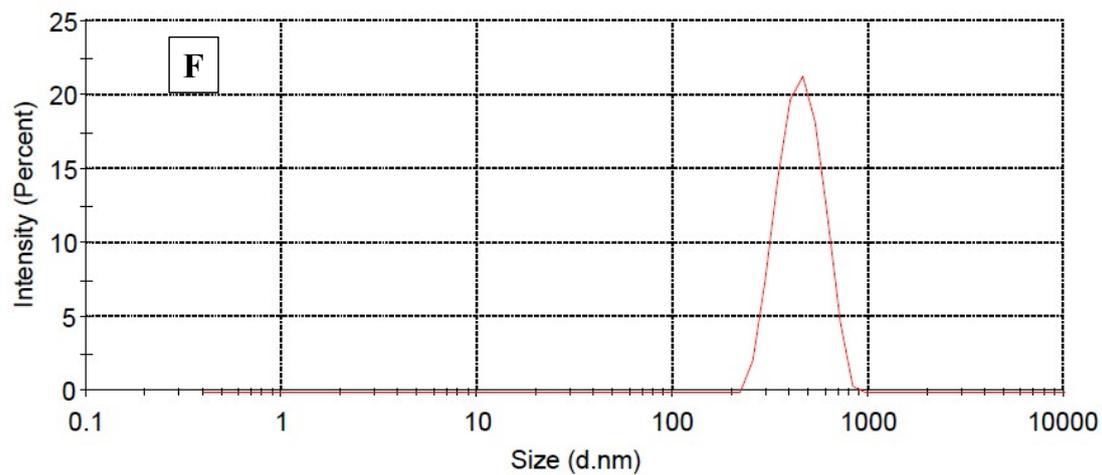
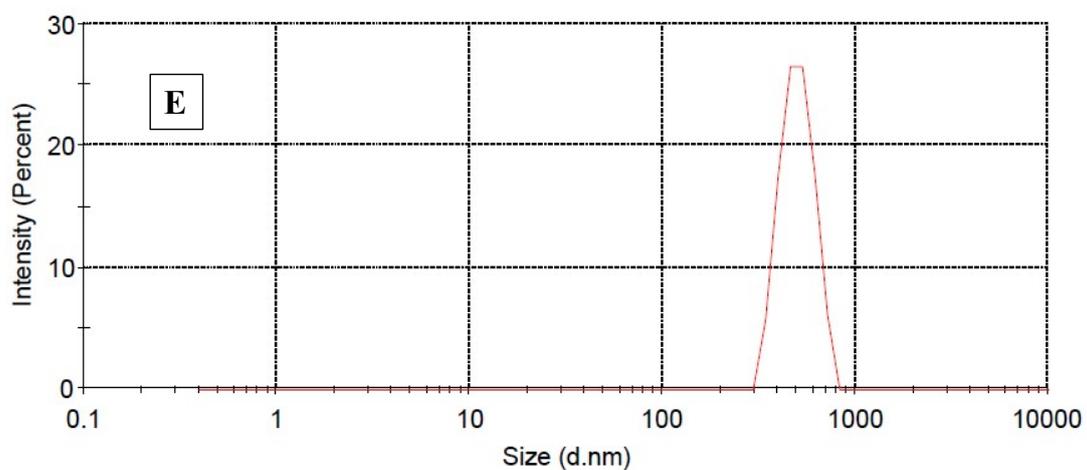
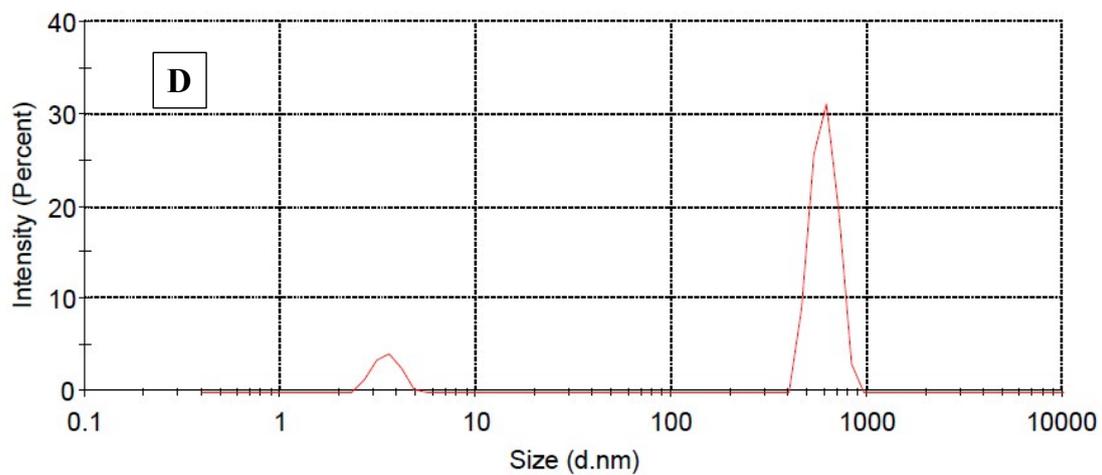


**Figure S19.**  $^1\text{H}$  NMR spectrum of polymer afforded at the feeding ratio of BEMP, MPEG-OH, U-1 and SAOCA to 0.25/1/1/150 (Table 1, Entry 9).

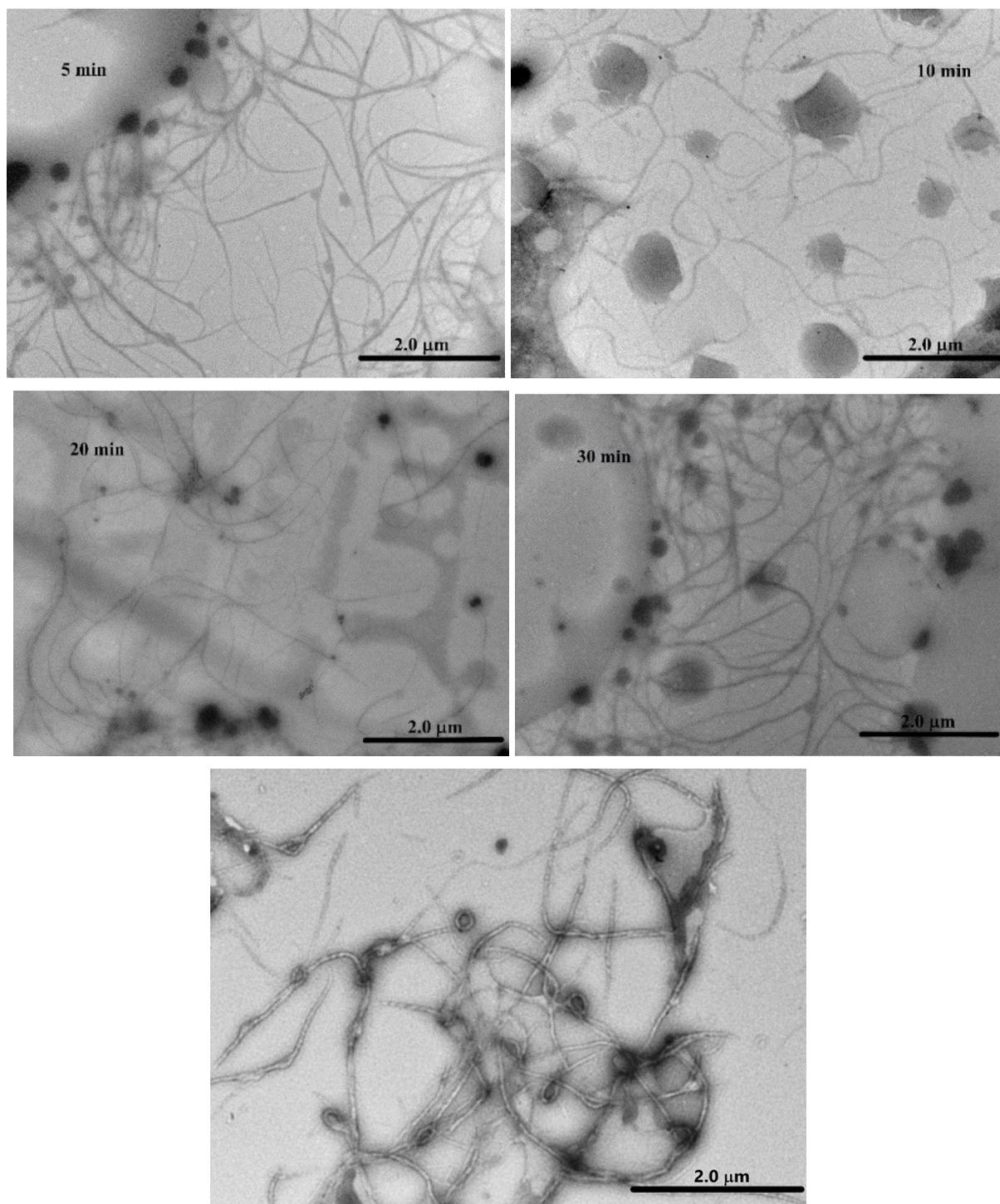


**Figure S20.** GPC trace of the resulting polymers via ROP of SAOCA using [BEMP]:[MPEG-OH]:[U-1]:[SAOCA] = 0.25:1:1:150 (Table 1, Entry 9).

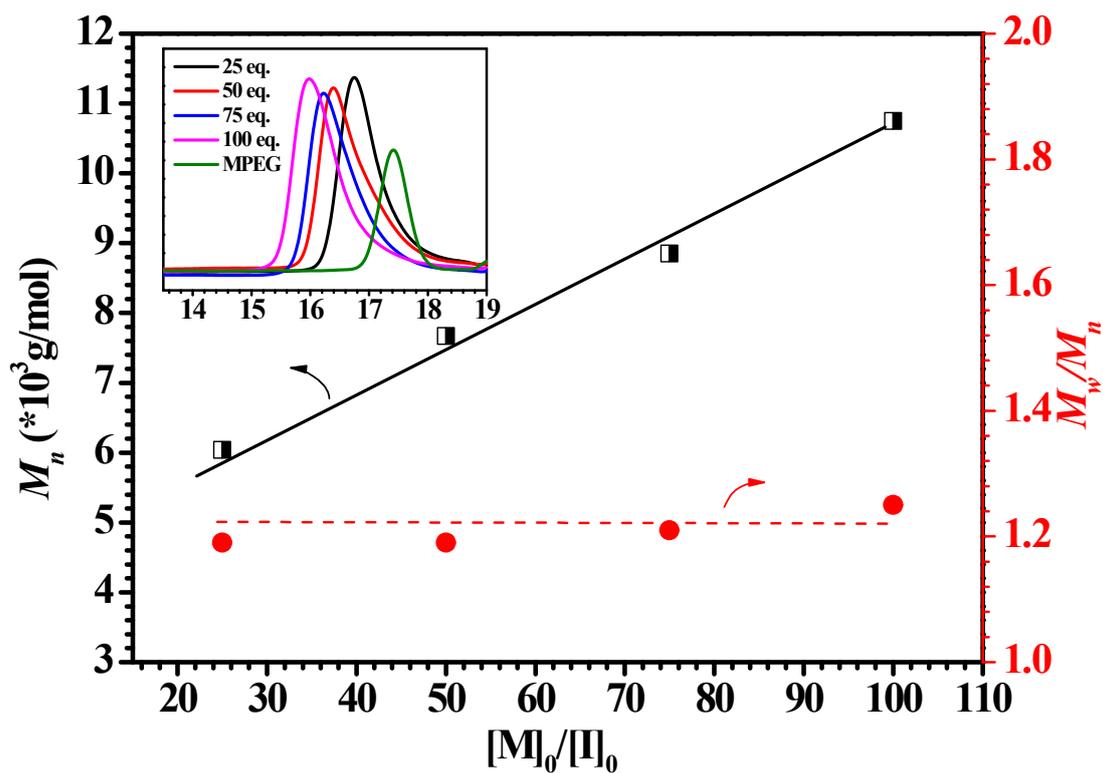




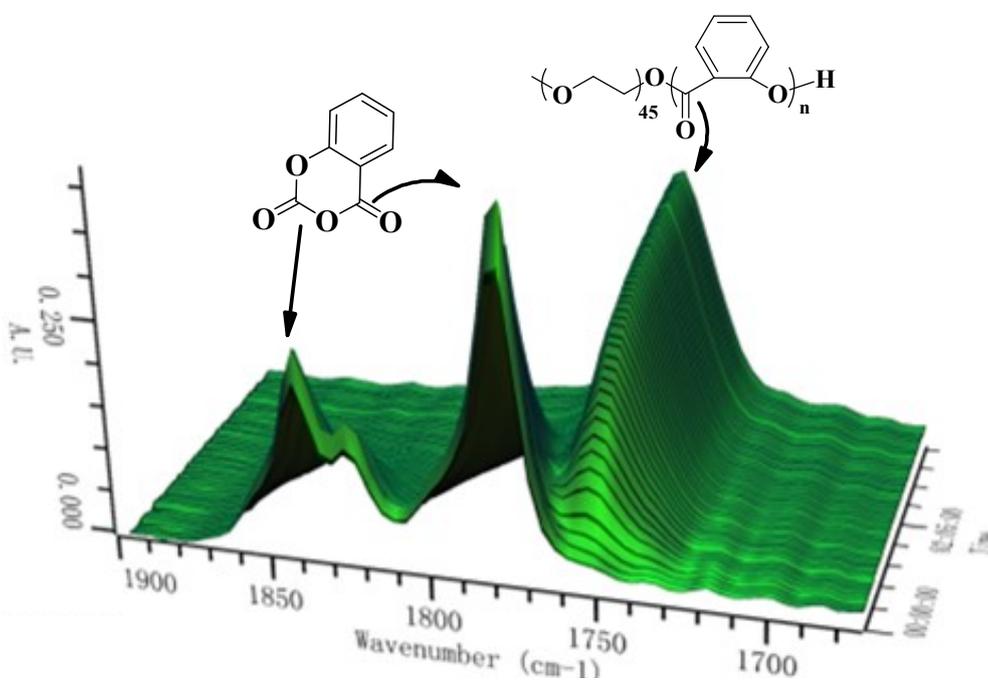
**Figure S21.** DLS diagram of the polymerization process of SAOCA, [BEMP]:[MPEG-OH]:[SAOCA] = 0.25:1:50, in THF at 25 °C, [SAOCA] = 0.75 M. (A) 5 min; (B) 10 min; (C) 20 min; (D) 30 min; (E) 40 min; (F) 50 min.



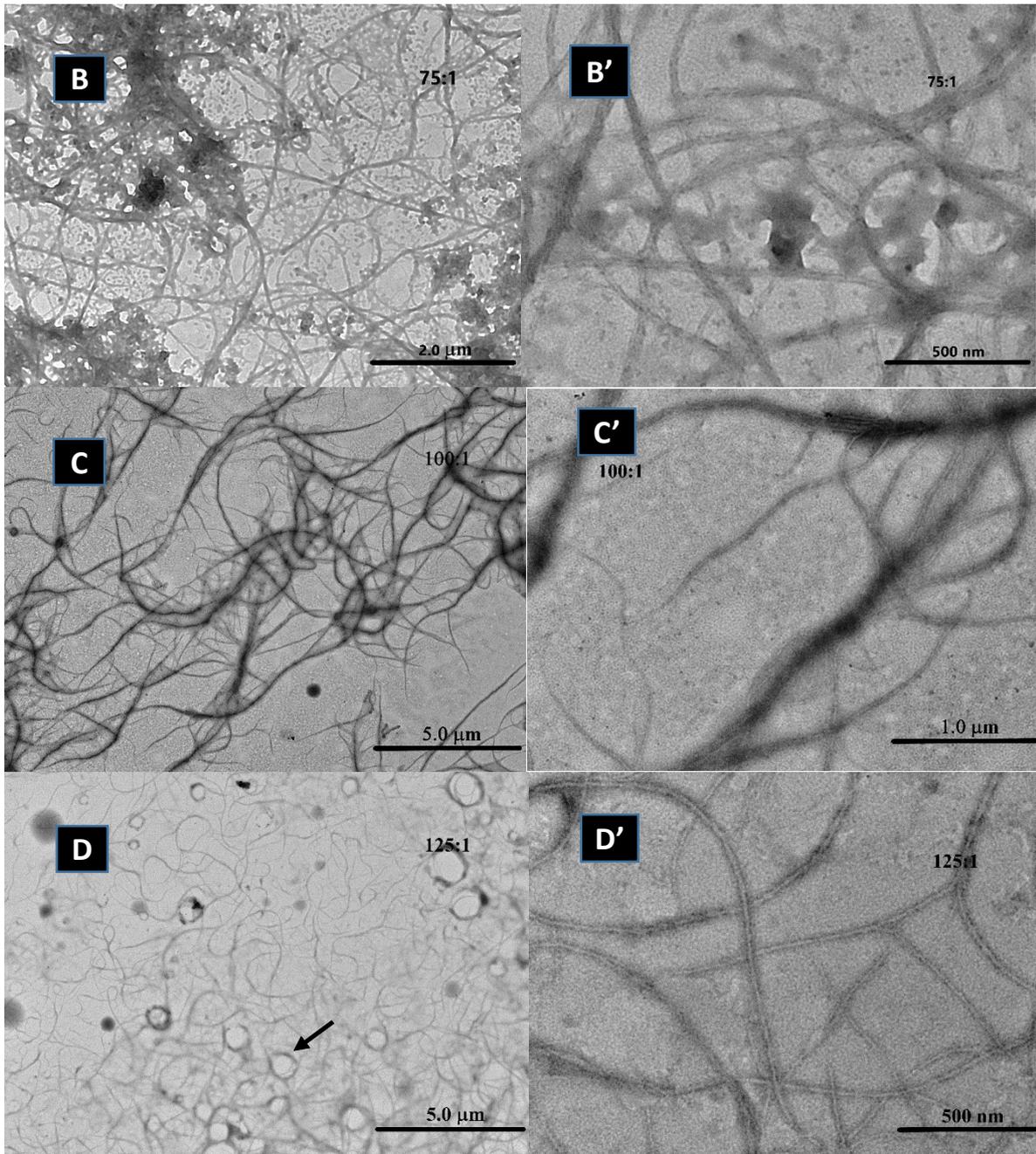
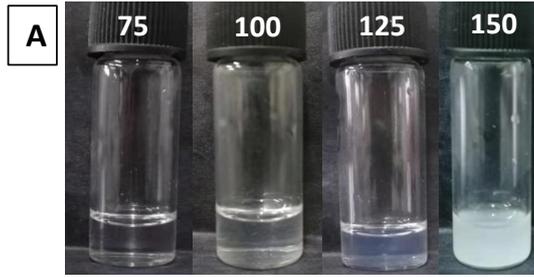
**Figure S22.** TEM image of MPEG-*b*-PSA carried out at the monomer-to-macroinitiator ratio of 50:1.

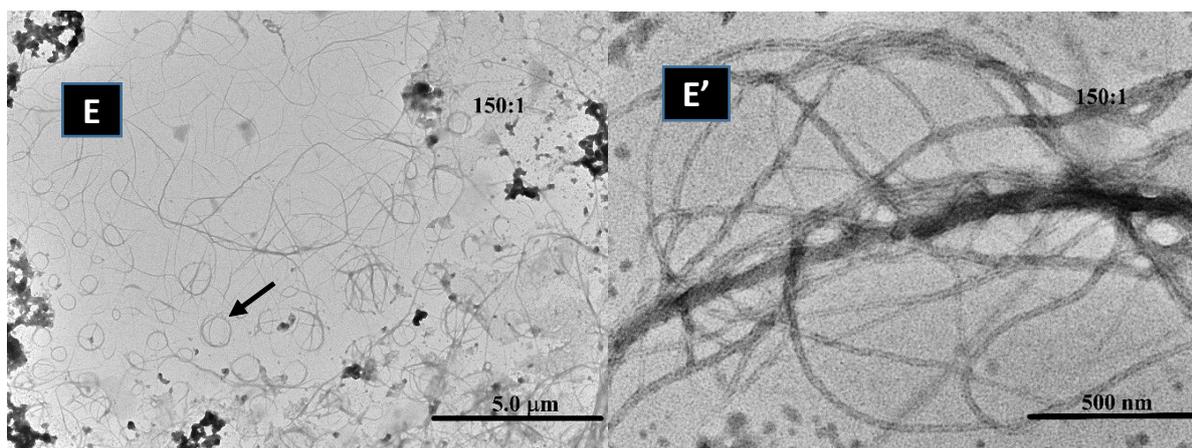


**Figure S23** (A) the corresponding plots of  $M_n$  and molecular weight distribution ( $\bar{D}$ ) versus  $[SAOCA]/[MPEGOH]$  ( $[BEMP]/[MPEG-OH] = 0.25:1$ ). Inset is GPC curves of the resulting polymers obtained with varied molar ratios of SAOCA to MPEGOH.

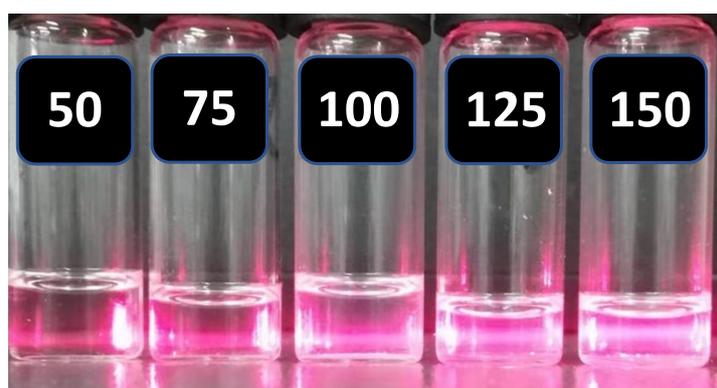


**Figure S24.** 3D kinetic behavior profile from *in situ* IR.





**Figure S25.** (A) Photos of ROPISA solutions by varying SAOCA feeding ratios the monomer-to-macroinitiator. TEM images carried out at the different the monomer-to-macroinitiator ratios (B) 75:1; (C) 100:1; (D) 125:1; (E) 150:1, and the corresponding zoomed in region (B')~(E').



**Figure S26.** Photos of PISA solution carried by varying the feeding ratios of SAOCA to MPEG in THF at 25 °C.  $[SAOCA] = 0.75 \text{ M}$ ,  $[BEMP]/[MPEG-OH]/[U-1] = 0.25/1/1$ . The rose-red light from the laser pointer passed through the ROPISA solution, and one bright light pillar was clearly observed due to Tyndall effect.