Electronic Supplementary Material (ESI) for Polymer Chemistry.


Supporting information

# ROPISA of salicylic acid *O*-carboxyanhydride: fast polymerization followed by in situ kinetics-driving self-assembly

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**S1. Materials.**

Triphosgene, activated carbon, anhydrous dichloromethane (DCM) and 1,5,7-Triazabicyclo[4.4.0]dec-5-ene (TBD) were purchased from INNOCHEM and used without treatment. Salicylic acid (SA) 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 ($M_n$ = 5000, mPEG-OH) purchased from INNOCHEM was azeotroped with toluene to remove water. $CDCl_3$ was purchased from Cambridge Isotope Laboratories. All the polymerization reactions were performed in a Vigor glove box.

**S2. Instrument and Characterization.**

The $^{1}H$ NMR analysis were carried out on a 400 MHz or 500 MHz NMR instrument (Bruker Corporation, Germany) at room temperature using $CDCl_3$ ($\delta$ = 7.26 ppm for $^{1}H$ 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 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 1747 $cm^{-1}$ and 1754 $cm^{-1}$, conversion% = $I_{1747}$ / ($I_{1747}$ + $I_{1754}$).

The morphology of the nanoparticles in THF (8.0 μL, 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.

The Hitachi U-3010 UV-Vis spectrophotometer was used to detect signal at 600 nm for turbidity measurement.

**S3. Synthesis procedure.**

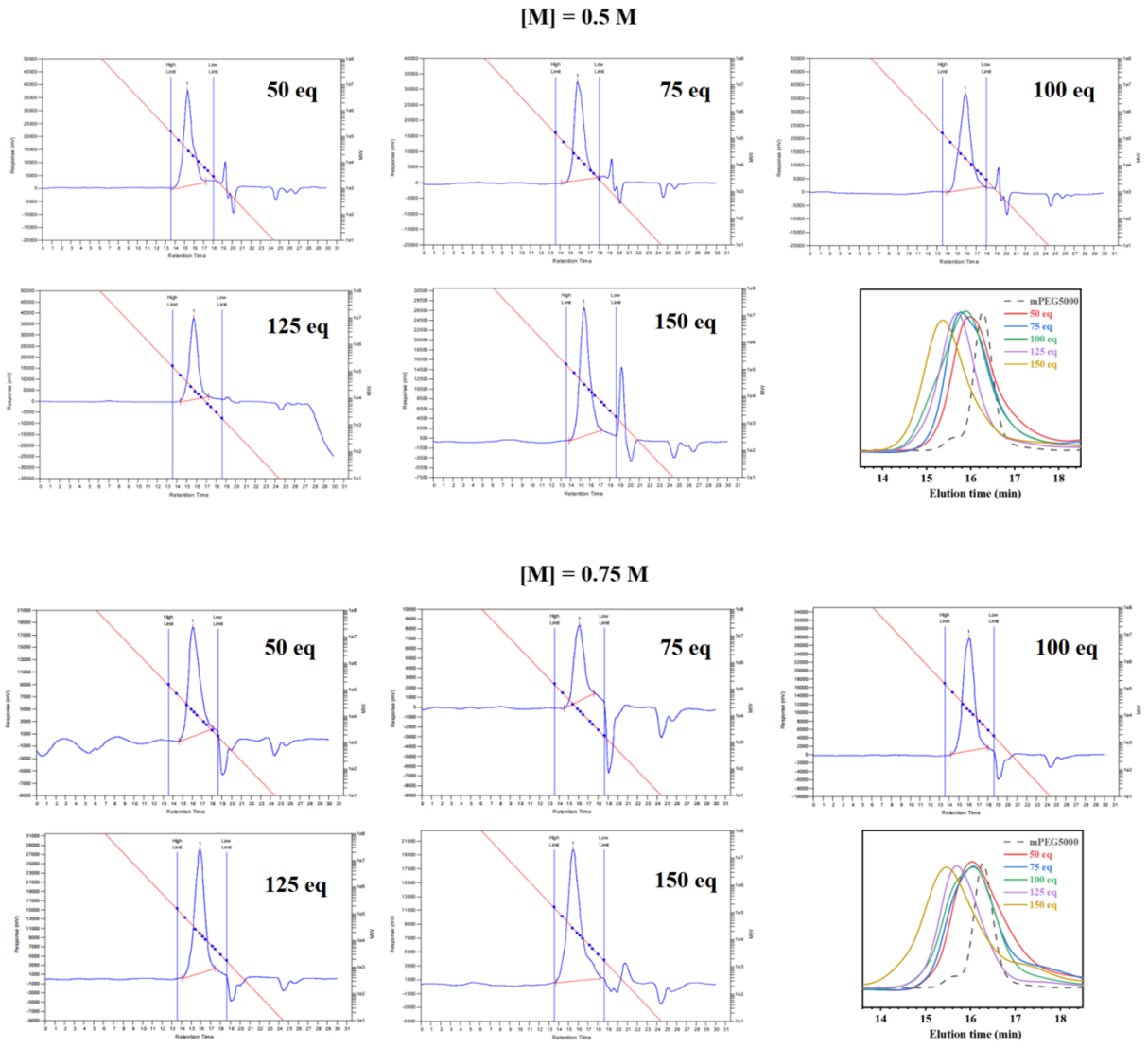
*Synthesis of SAOCA monomer.*

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 $MgSO_4$. 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%.$^1$H NMR (400 MHz, $CDCl_3$), δ (ppm): 8.10 (*d*, *J* = 7.8 Hz, 1H, *Ar*H), 7.84 (*t*, *J* = 7.9 Hz, 1H, *Ar*H), 7.46 (*t*, *J* = 7.6 Hz, 1H, *Ar*H), 7.34 (*d*, *J* = 8.4 Hz, 1H, *Ar*H). $^{13}$C NMR ($CDCl_3$, 125 MHz), δ (ppm): 155.71 (C=O), 153.81 (*Ar*C), 142.15 (OC=OO), 138.67 (*Ar*C), 130.08 (*Ar*C), 126.78 (*Ar*C), 116.82 (*Ar*C), 109.83 (*Ar*C).

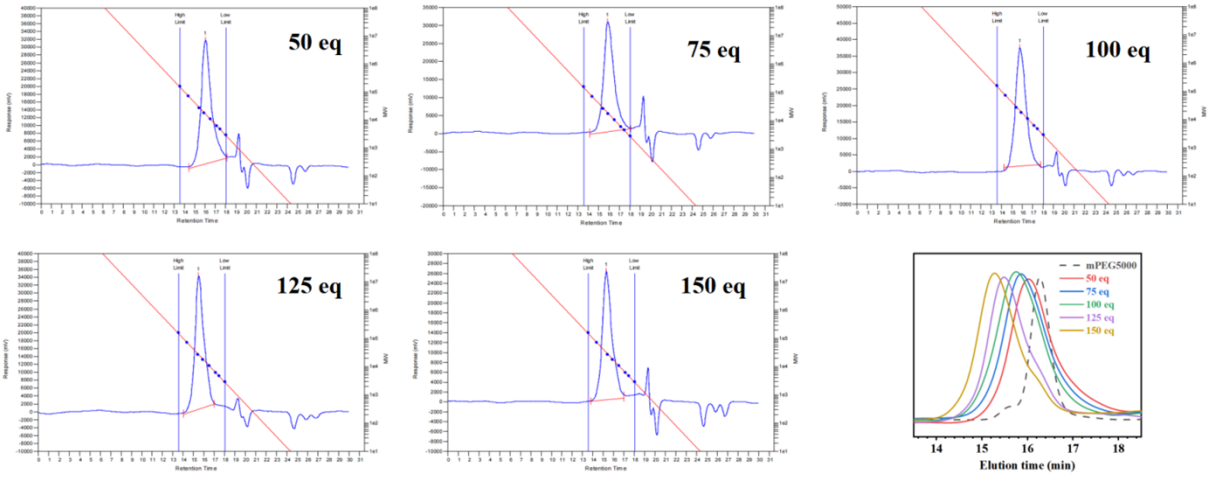
*Polymerization procedure.*

A typical procedure for polymerization of SAOCA was performed in a 25 mL Schlenk in a Vigor glovebox. The determined amount of TBD 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.

## S4. Supplementary GPC results



**[M] = 1.0 M**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150 eq
Elution time (min)

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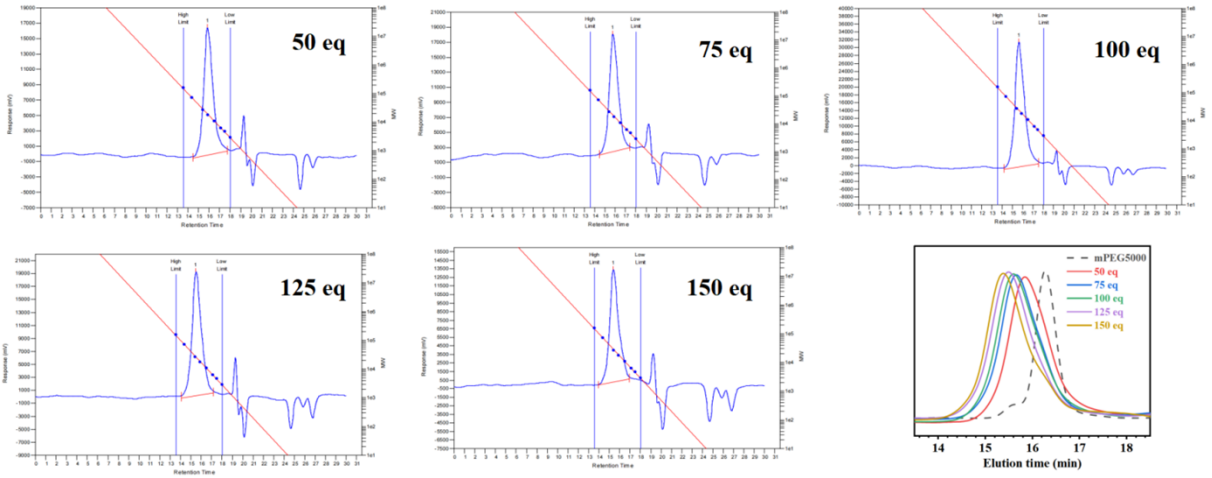
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75 eq
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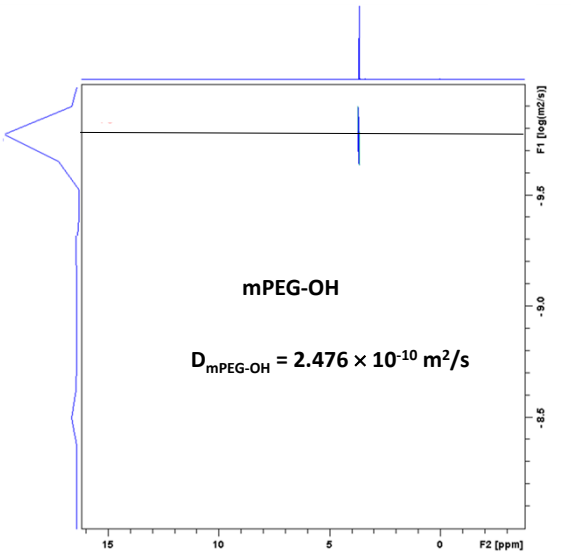
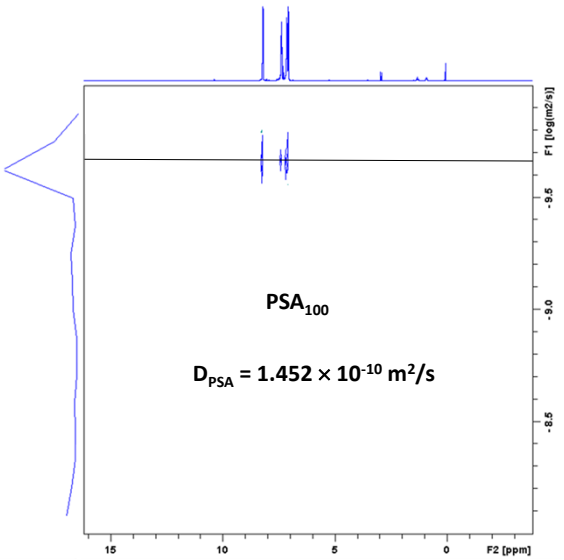
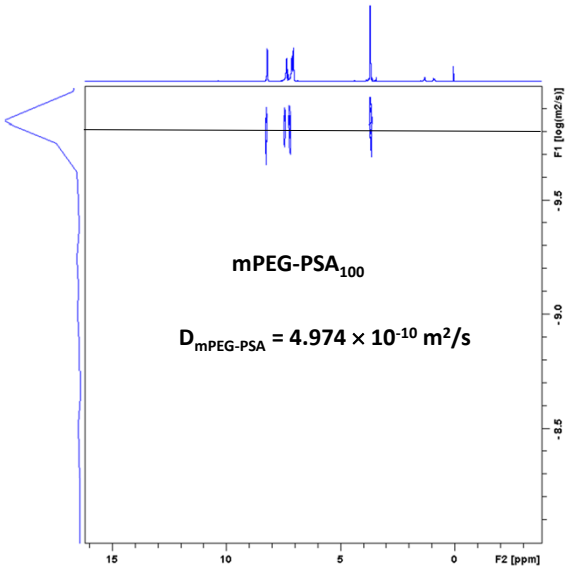
125 eq
150 eq
mPEG5000
50 eq
75 eq
100 eq
125 eq
150 eq
Elution time (min)

**S5. DOSY results.**



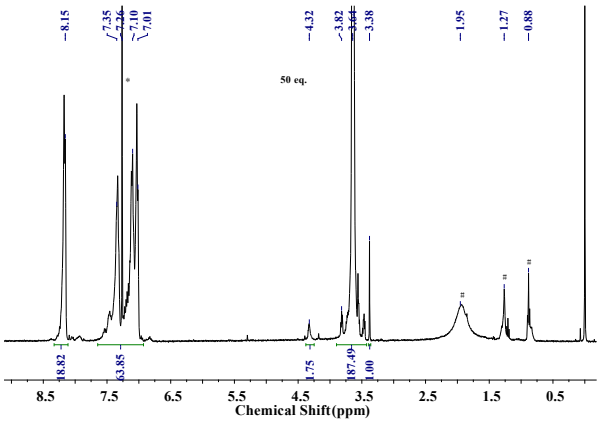



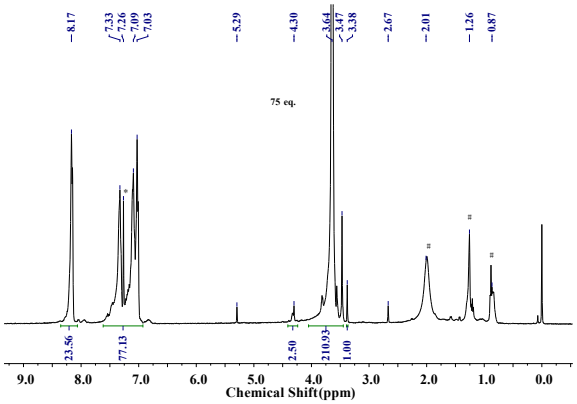



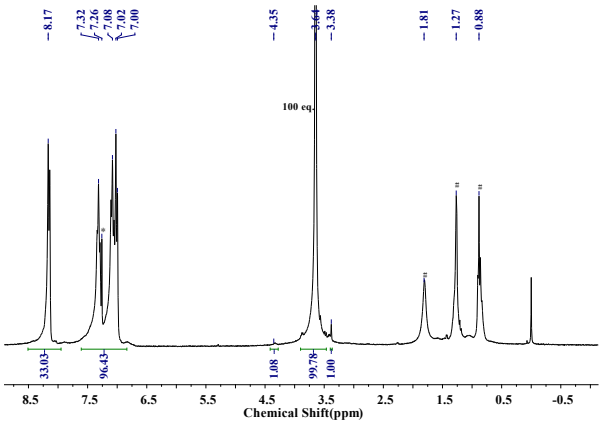
## S6. Supplementary $^{1}$H NMR results

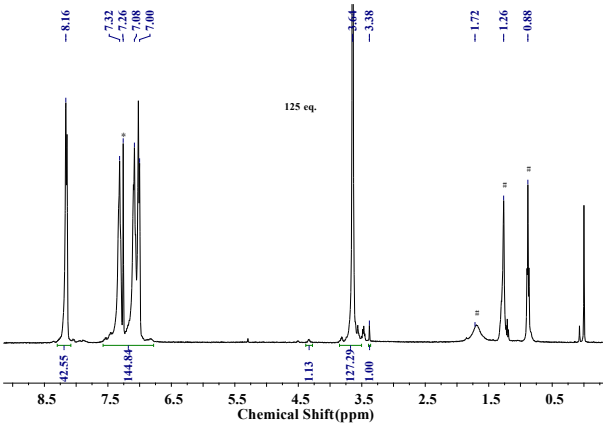
*stands for $CDCl_3$; # (the peaks appear 1.26 and 0.87 ppm) represents the signals from hexane, and other well numbers showing at 2.01 ppm 5.29 ppm are probably associated with solvents such as $H_2O$ and $CH_2Cl_2$.

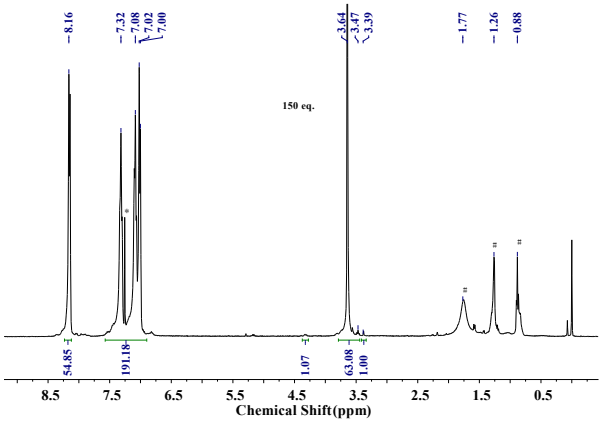
**[M] = 0.5 M**



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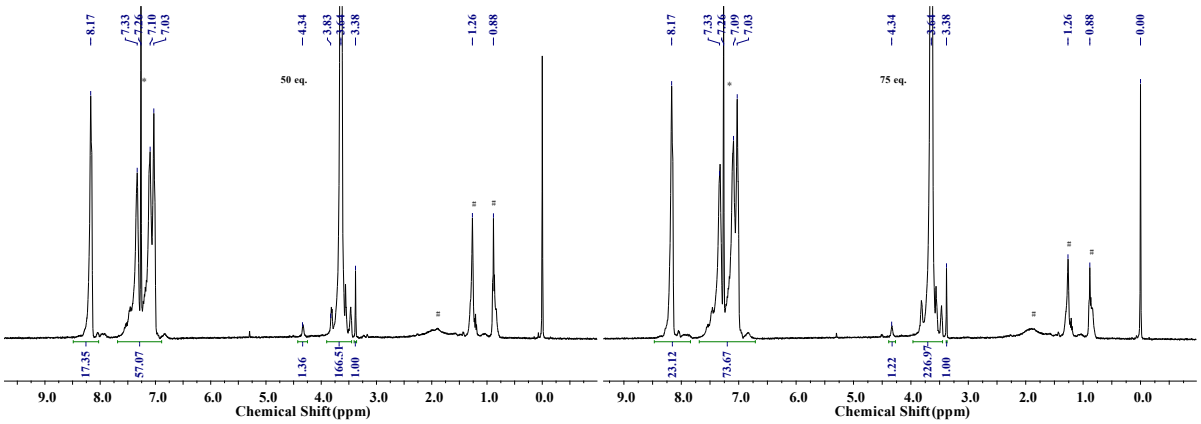
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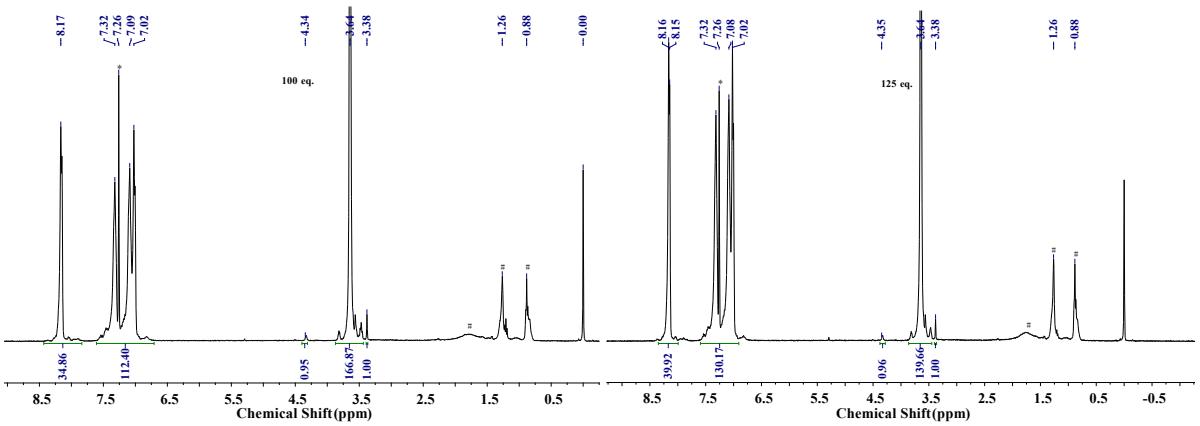
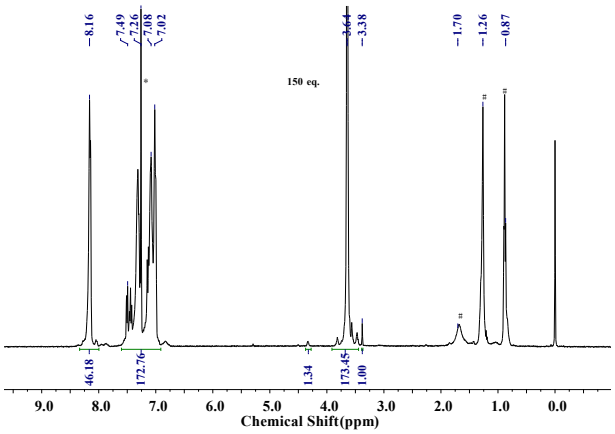

100 eq.
125 eq.
Chemical Shift(ppm)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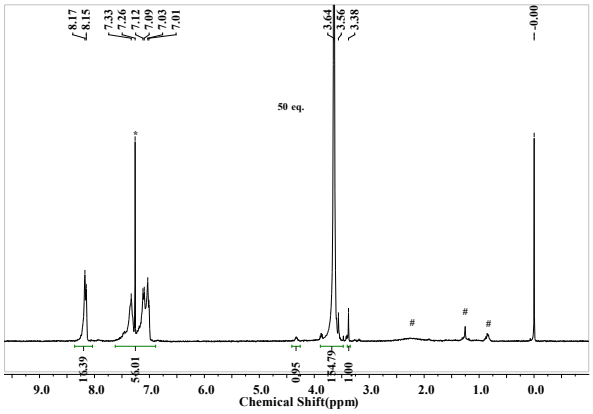
Chemical Shift(ppm)

**[M] = 1.0 M**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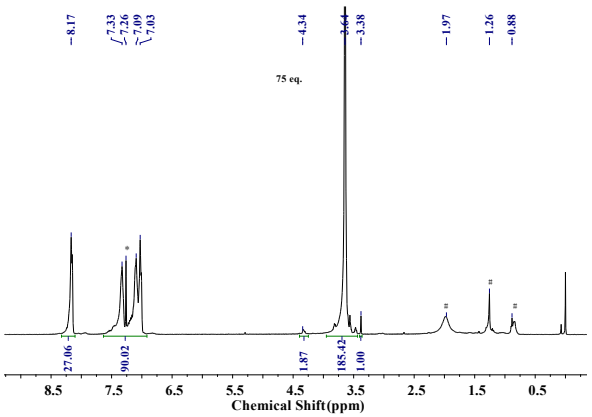
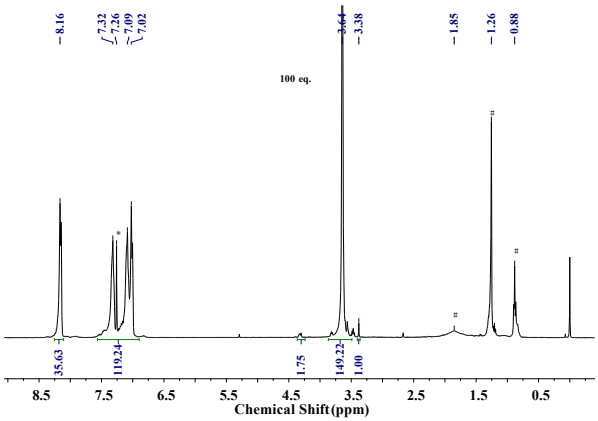
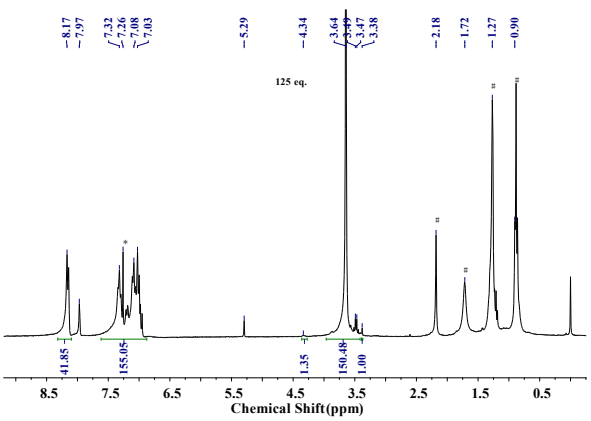
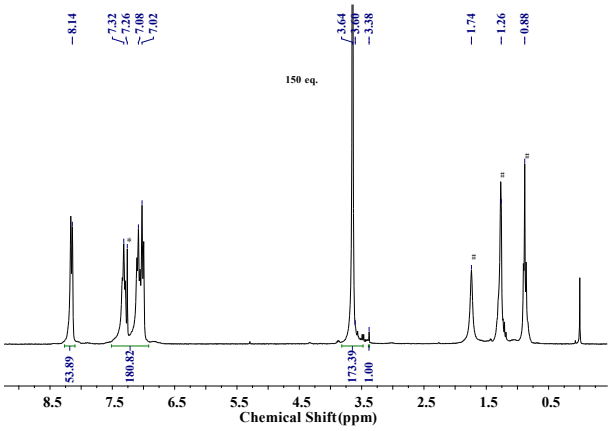
Chemical Shift(ppm)


75 eq.
Chemical Shift(ppm)


100 eq.
Chemical Shift(ppm)


125 eq.
Chemical Shift(ppm)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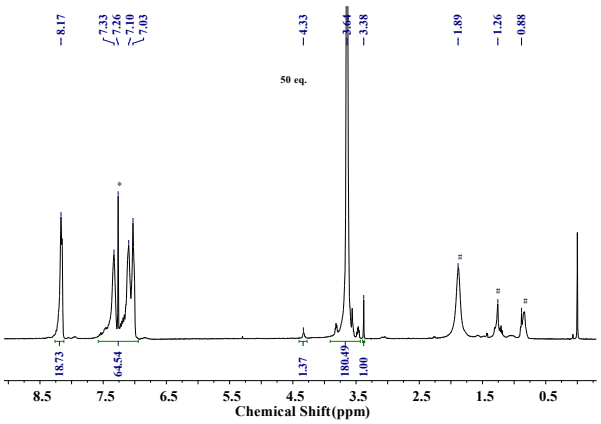
Chemical Shift(ppm)

**[M] = 1.25 M**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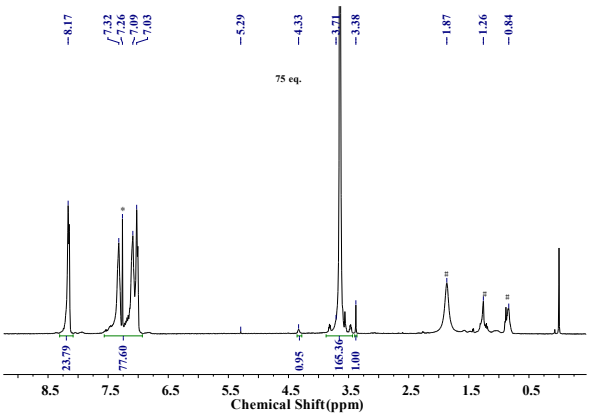
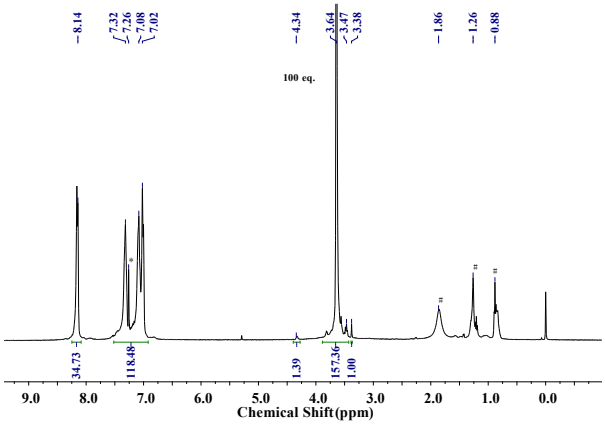
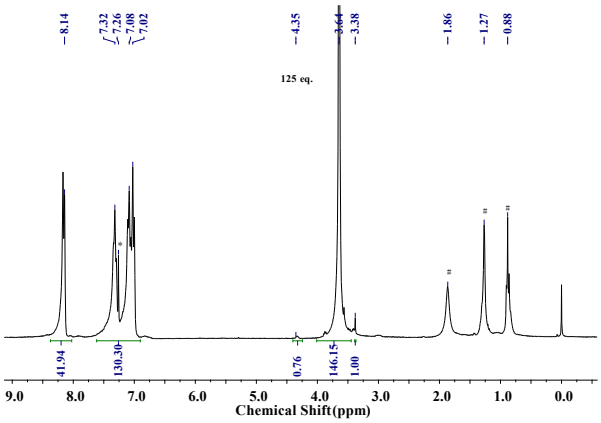
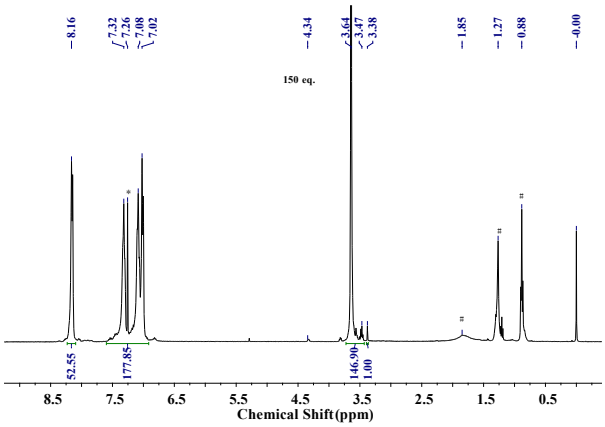
7.33
7.26
7.10
7.03
4.33
3.64
3.38
1.89
1.26
0.88
50 eq.
18.73
64.54
1.37
180.49
1.00
Chemical Shift(ppm)


8.17
7.32
7.26
7.09
7.03
5.29
4.33
3.71
3.38
1.87
1.26
0.84
75 eq.
23.79
77.60
0.95
165.36
1.00
Chemical Shift(ppm)


8.14
7.32
7.26
7.08
7.02
4.34
3.64
3.47
3.38
1.86
1.26
0.88
100 eq.
34.73
118.48
1.39
157.36
1.00
Chemical Shift(ppm)


8.14
7.32
7.26
7.08
7.02
4.35
3.64
3.38
1.86
1.27
0.88
125 eq.
41.94
130.30
0.76
146.15
1.00
Chemical Shift(ppm)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7.32
7.26
7.08
7.02
4.34
3.64
3.47
3.38
1.85
1.27
0.88
0.00
150 eq.
52.55
177.85
146.90
1.00
Chemical Shift(ppm)

## S7. Supplementary Figures

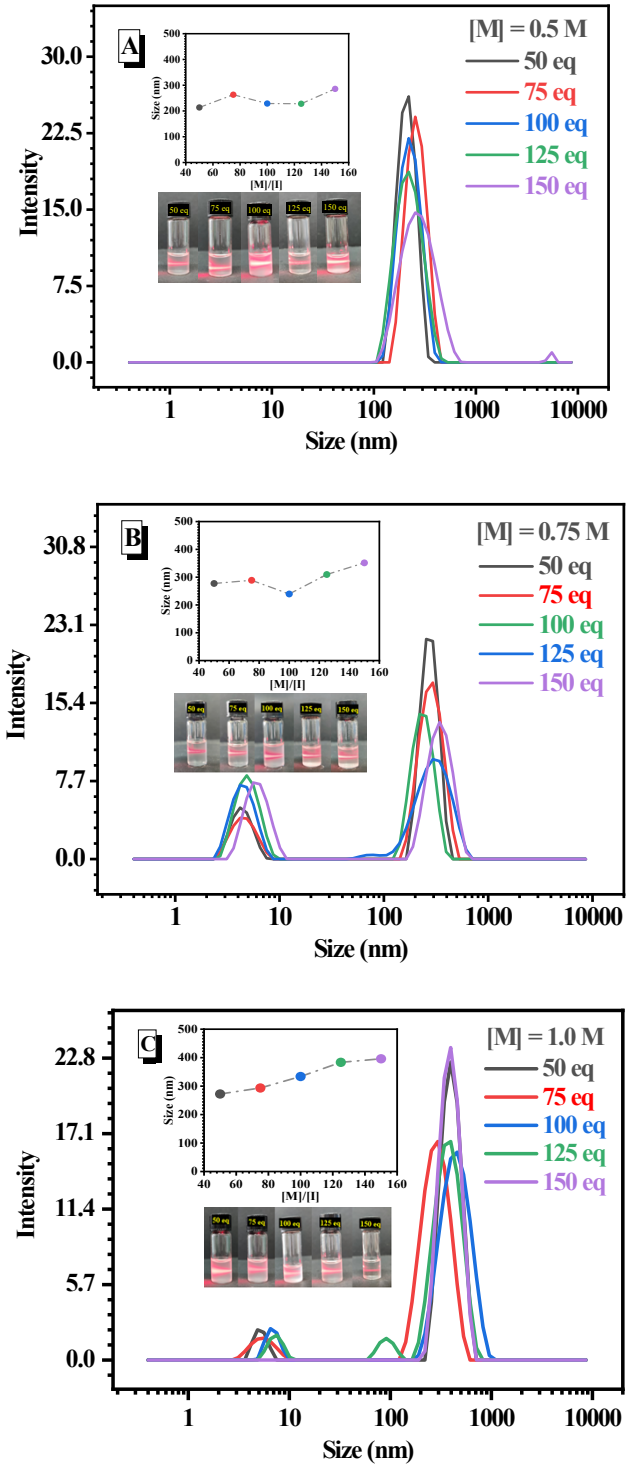
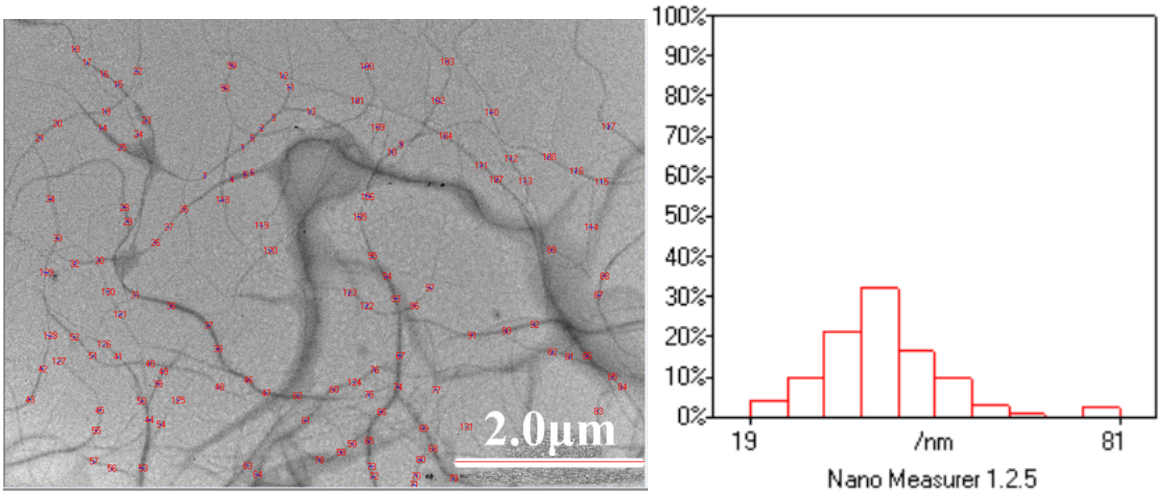



**Figure S1**. DLS diagrams of nanoparticles via ROPISA of SAOCA varying [M]/[I] and SAOCA concentrations, (A) [M] = 0.5 M; (B) [M] = 0.75 M; (C) [M] = 1.0 M. The insets are the nanoparticle sizes and the photos of ROPISA solutions dependence of the different monomer-to-macroinitiator ratios.

**[SAOCA] = 0.75 M, [SAOCA]/[I] = 100/1**




**[SAOCA] = 1.2 M, [SAOCA]/[I] = 100/1**

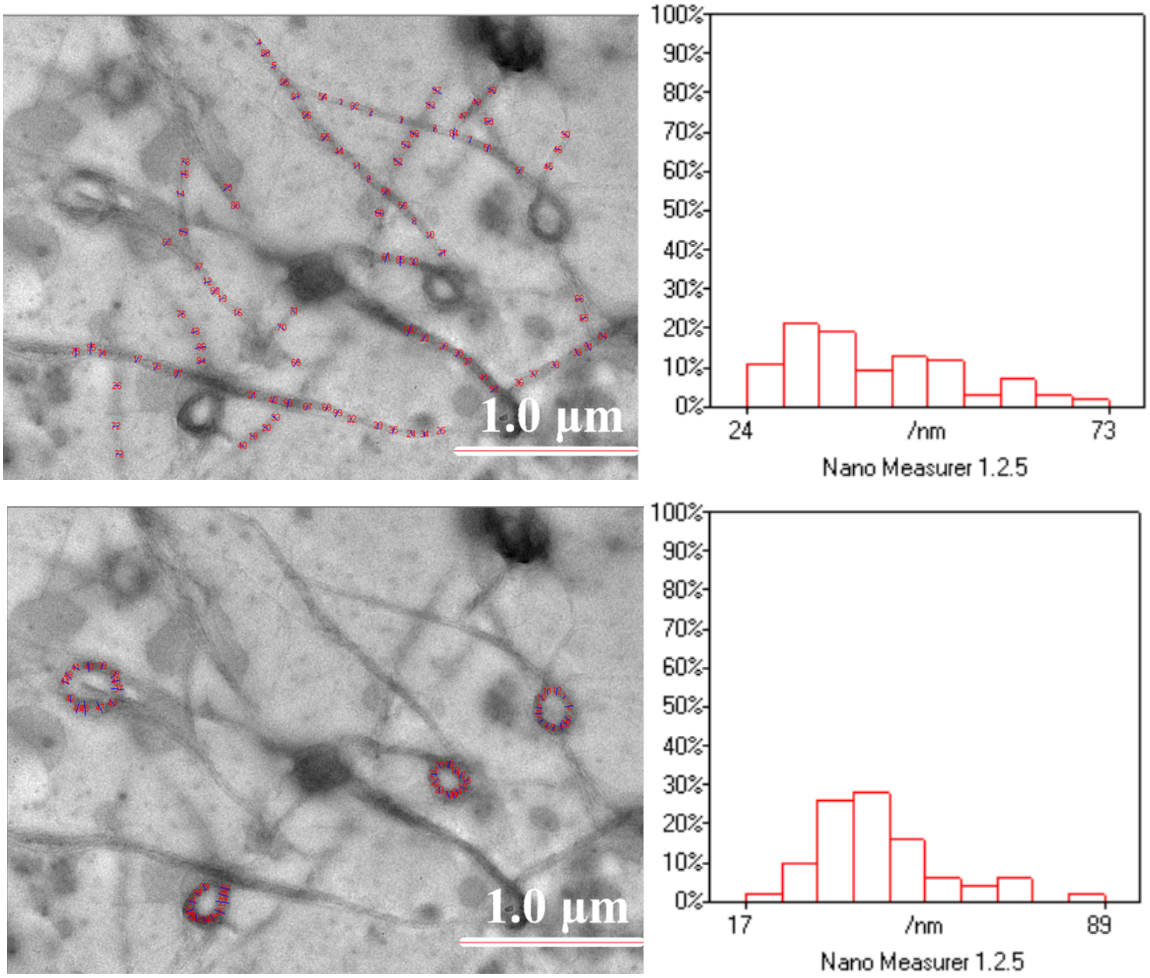



**Figure S2**. Presentative examples of randomly selecting nanoparticles in TEM image (Left) and statistical average size of nanoparticles (right)

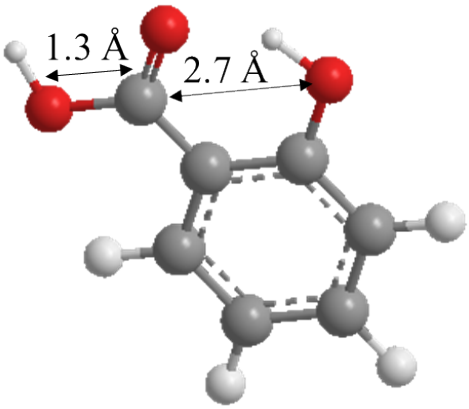



**Figure S3**. The image of the atom distance in SA repeating unit simulated by 3D Chemdraw software.

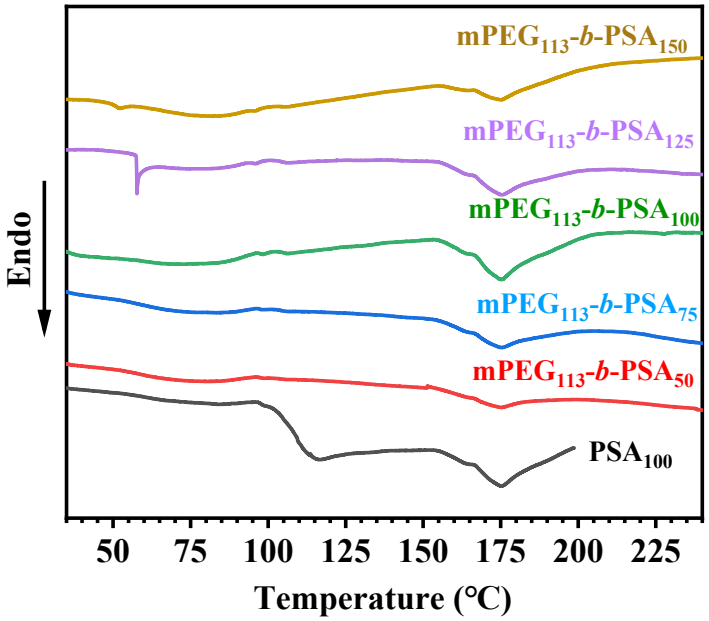



**Figure S4**. DSC traces of mPEG-PSA block copolymers during the second time heating at 10 °C /min.

## S8. Supplementary Tables

**Table S1**. The thermal properties of the block copolymers mPEG-*b*-PSA.

| Entry | Block polymer | TGA (°C) | | | DSC | | |
|---|---|---|---|---|---|---|---|
| | | $T_{d\text{-}5\%}$ | $T_{max1}$ | $T_{max2}$ | $T_g$ (°C) | $T_m$ (°C) | ΔH (J/g) |
| 1 | $PSA_{100}$ | 300.26 | 409.47 | --- | 109.33 | 165.74 | 1.107 |
| 2 | $mPEG_{113}$-$PSA_{50}$ | 328.63 | 411.70 | 444.73 | --- | 161.21 | 1.019 |
| 3 | $mPEG_{113}$-$PSA_{75}$ | 326.80 | 398.10 | 445.30 | --- | 161.08 | 2.437 |
| 4 | $mPEG_{113}$-$PSA_{100}$ | 316.17 | 362.85 | 420.85 | --- | 163.21 | 4.995 |
| 5 | $mPEG_{113}$-$PSA_{125}$ | 322.72 | 396.40 | 423.79 | --- | 162.42 | 3.187 |
| 6 | $mPEG_{113}$-$PSA_{150}$ | 328.80 | 398.67 | 437.91 | --- | 163.74 | 2.837 |