

*Supporting Information for*

**Efficient preparation of cyclic polymers via pre-stacking of photo-cycloadditionable end groups and a continuous-flow technique**

Leiyu Chen,<sup>#</sup> Xiang Wang,<sup>#</sup> Ruijie Hou, Haipeng Lu, Zhenbi He, Xianjing Zhou,<sup>\*</sup> Wei Zhang, and Xinping Wang<sup>\*</sup>

School of Chemistry and Chemical Engineering, Key Laboratory of Surface & Interface Science of Polymer Materials of Zhejiang Province, Zhejiang Sci-Tech University, Hangzhou 310018, China

---

<sup>#</sup> These authors contributed equally to this work.

<sup>\*</sup> Corresponding author.

Xianjing Zhou (E-mail: [xjzhou@zstu.edu.cn](mailto:xjzhou@zstu.edu.cn)) & Xinping Wang (E-mail: [wxinping@zstu.edu.cn](mailto:wxinping@zstu.edu.cn))

## Experimental section

### Materials

1-Bromopyrene (Energy Chemical, 95%), 4-vinyl benzoic acid (Energy Chemical, 96%), triphenylphosphine (PPh<sub>3</sub>, Energy Chemical, 98%), triethylamine (TEA, Macklin, 99%), palladium (II) acetate (Pd(OAc)<sub>2</sub>, Sigma-Aldrich, 99.9%), ammonium chloride (NH<sub>4</sub>Cl, Macklin, 99.5%), anhydrous magnesium sulfate (MgSO<sub>4</sub>, Macklin, 99%), calcium hydride (CaH<sub>2</sub>, Macklin, 97%), dimethyl 2,6-dibromoheptanedioate (DMDBHD, Macklin, 98%), ethylene bis(2-bromoisobutyrate) (Macklin, 97%), N,N,N',N'',N''-pentamethyldiethylenetriamine (PMDETA, Aladdin, 99%), sodium azide (NaN<sub>3</sub>, Sigma-Aldrich, 99.5%), 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD, Aladdin, 98%), 1,8-octanediol (Aladdin, 98%), 4-dimethylaminopyridine (DMAP, Aladdin, 99%), polyethylene oxide (HO-PEO<sub>90</sub>-OH,  $M_n = 4000$ , Aladdin), 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC·HCl, Energy Chemical, 99%), N,N-diisopropylethylamine (DIEA, Aladdin, 99%), 1-hydroxybenzotriazole (HOBT, Macklin, 97%), sodium bicarbonate (NaHCO<sub>3</sub>, Macklin, 99.5%), sodium chloride (NaCl, Macklin, 99.5%), chloroform-d (CDCl<sub>3</sub>, Macklin, 99.8%) and cyclohexane (Aladdin, 99.5%) were used directly as received. Styrene (St, Aladdin, 99%) was distilled under reduced pressure to remove the inhibitor before use. Copper(I) bromide (CuBr, Macklin, 98%) was washed with glacial acetic twice, ethanol twice, and ethyl ether twice and then dried in vacuum overnight and stored under vacuum before use. The  $\epsilon$ -caprolactone ( $\epsilon$ -CL, Aladdin, 99%) was stirred overnight with calcium hydride, and freshly distilled prior to polymerization into a flask containing activated molecular sieves. All other solvents, such as dichloromethane (DCM), tetrahydrofuran (THF), ethylacetate (EtOAc), methanol (MeOH), ethyl ether (Et<sub>2</sub>O), toluene and N, N-dimethylformamide (DMF) were purchased from Hangzhou Shuanglin Chemical Reagent Co. and used directly as received.

### Synthesis of carboxy-styrylpyrene (SP-COOH)

1-Bromopyrene (2.9212 g, 10.4 mmol), 4-vinyl benzoic acid (1.4931 g, 10.1 mmol) and

triphenylphosphine (53.3 mg, 0.2 mmol) were dissolved in a mixed solvent of N,N-dimethylformamide (DMF) and TEA (45 mL,  $v_{\text{DMF}} : v_{\text{TEA}} = 2 : 1$ ). The solution was degassed with  $\text{N}_2$  for 30 min and  $\text{Pd}(\text{OAc})_2$  (27.0 mg, 0.1 mmol) was then added. The mixture was heated to 100 °C and stirred overnight. The solution was then allowed to cool to ambient temperature and diluted with saturated  $\text{NH}_4\text{Cl}$  solution (200 mL). The solid was filtered and dissolved in tetrahydrofuran (THF). The solution was dried over anhydrous  $\text{MgSO}_4$ , filtered, and the mixture concentrated until only a small amount of THF was left and precipitated into cold diethyl ether. The crude product was purified by column chromatography on silica gel and running with dichloromethane/methanol ( $v/v = 10:1$ ) to give a solid yellow product (yield: 2.48 g, 68%). The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of SP-COOH are shown in Fig. S1. HRMS(ESI):  $m/z$  calculated for  $\text{C}_{25}\text{H}_{17}\text{O}_2^+$   $[\text{M}+\text{H}]^+$ : 349.1223; measured: 349.1240.

### **Synthesis of telechelic polystyrene with amino end groups**

Telechelic polystyrene with amino end groups ( $\text{NH}_2\text{-PSt-NH}_2$ ) was synthesized through atom transfer radical polymerization (ATRP) and a series of end group functionalization steps, as shown in Fig. S2.

### **Synthesis of $\alpha,\omega$ -bromine-terminated polystyrene (Br-PSt-Br) by ATRP**

For dimethyl 2,6-dibromoheptanedioate as an initiator, the ATRP of styrene (St) under  $[\text{St}]/[\text{DMDBHD}]/[\text{CuBr}]/[\text{PMDETA}] = 20:1:0.2:0.2$  at 100 °C is typically described as follows. To a previously dried cock-attached 50 mL flask equipped with a magnetic stirring bar, styrene, DMDBHD, and PMDETA were added and stirred under a nitrogen atmosphere. The mixed solution was degassed with freezing-pumping-thawing cycles three times, and CuBr was added under a nitrogen atmosphere. The freezing-pumping-thawing cycle was then repeated. After the CuBr was completely dissolved, the reactor was immersed into an oil bath that had been preheated to 100 °C and polymerized for a pre-set time. After that, the reaction was terminated by freezing with liquid nitrogen. The reaction mixture was diluted with THF and passed through a column filled with neutral alumina (100-200 mesh) to remove the catalyst. The obtained solution was

concentrated by rotary evaporation and precipitated with methanol three times. Finally, the precipitates were dried at 40 °C under vacuum overnight to give white powders.

For ethylene bis(2-bromoisobutyrate) as an initiator, the ATRP of styrene (St) under  $[\text{St}]/[\text{Ethylene bis(2-bromoisobutyrate)}]/[\text{CuBr}]/[\text{PMDETA}] = 200:1:2:2$  at 90 °C reaction for a set time, and the remaining steps were basically the same as per the previous synthesis.

To ensure a high degree of chain-end functionality, the monomer conversion was controlled to below 30%. The number-average molecular weight, polymer dispersity index and conversion of the Br-PSt-Br are listed in Table S1.

#### **Synthesis of $\alpha,\omega$ -azide-terminated polystyrene ( $\text{N}_3\text{-PSt-N}_3$ )**

Br-PSt-Br (2.5 g, 0.86 mmol) and  $\text{NaN}_3$  (0.56 g, 8.6 mmol) were dissolved in 20 mL of DMF. The mixture was stirred overnight at room temperature, and the polymer was isolated through precipitation in methanol three times to remove the NaBr and unreacted  $\text{NaN}_3$ . The product was filtered and dried under vacuum at 40 °C. The number-average molecular weight, polymer dispersity index and conversion of the  $\text{N}_3\text{-PSt-N}_3$  are listed in Table S1.

#### **Synthesis of $\alpha,\omega$ -amine-terminated polystyrene ( $\text{NH}_2\text{-PSt-NH}_2$ )**

$\text{N}_3\text{-PSt-N}_3$  (2.0 g, 0.68 mmol) and  $\text{PPh}_3$  (0.90 g, 3.4 mmol) were dissolved in 20 mL of dry THF, the mixture was stirred overnight at room temperature. Then, 10 ml water was added, and the reaction mixture was stirred at 60 °C for 24h. Rotary evaporation of the solvent gave a residue, which was purified through precipitation in methanol. The product was filtered and dried under vacuum at 40 °C. The number-average molecular weight, polymer dispersity index and conversion of the  $\text{NH}_2\text{-PSt-NH}_2$  are listed in Table S1.

#### **Synthesis of polycaprolactone diol (HO-PCL-OH)**

In a representative polymerization, TBD (0.07 g, 0.5 mmol) and 1,8-octanediol (0.29 mg, 2 mmol) were dissolved in toluene (20 mL) first, and the traces of water in the

solution were removed by azeotroping with toluene under vacuum. Then,  $\epsilon$ -CL (11.41 g, 100 mmol) was added to the system and stirred at room temperature. Depending on the desired molecular weight, the polymerization could be stopped by addition of benzoic acid. The crude solution of polymer was precipitated into diethyl ether, filtered, and dried *in vacuo*. The SEC elution traces,  $^1\text{H}$  NMR spectra, and the mass determination of HO-PCL-OH are shown in Fig. S6 and Table S2.

### **Synthesis of telechelic polymers with styrylpyrenyl end groups (SP-polymer-SP)**

#### **Synthesis of $\alpha,\omega$ -styrylpyrene-terminated PSt (SP-PSt-SP)**

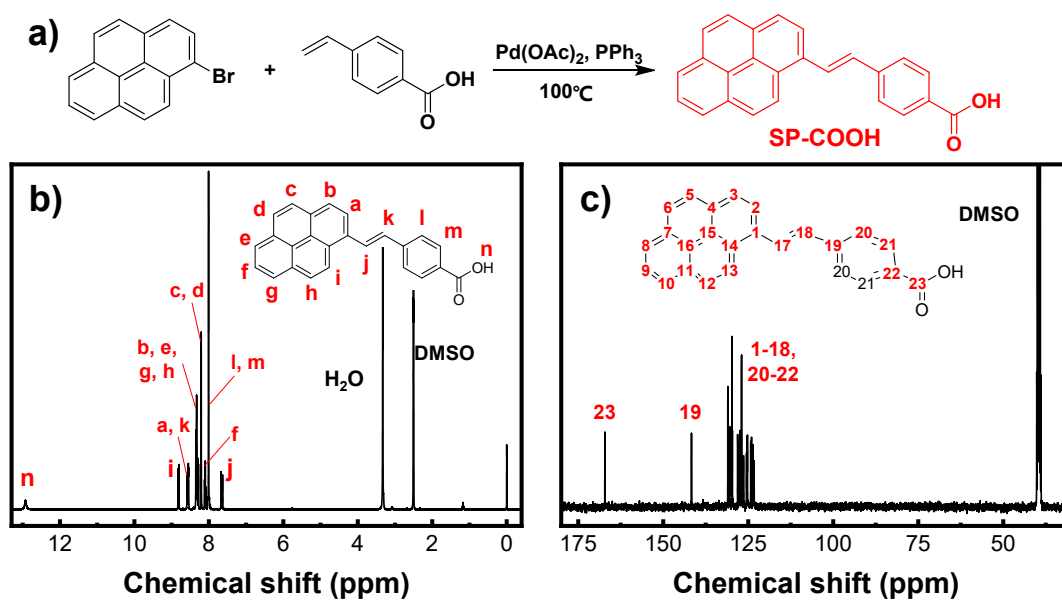
Telechelic polystyrene with styrylpyrenyl end groups, *i.e.*, SP-PSt-SP was synthesized by amidation reaction between  $\text{NH}_2\text{-PSt-NH}_2$  and slightly excessive SP-COOH, as shown in Fig. S2. The typical experimental process was as follows: SP-COOH (0.21 g, 0.6 mmol, 3 eq), EDC·HCl (5.8 mg, 0.3 mmol, 1.5 eq), HOBT (0.04 g, 0.3 mmol, 1.5 eq) and DIEA (100  $\mu\text{L}$ , 0.6 mmol, 3 eq) were dissolved in 12 mL of DMF and cooled in an ice bath. Then  $\text{NH}_2\text{-PSt}_{26}\text{-NH}_2$  (0.7 g, 0.2 mmol, 1 eq) was added to the reaction mixture, which was stirred at 25  $^\circ\text{C}$  for 48 h. The product was diluted with a small amount of EtOAc, and the organic layer was washed with a saturated aqueous solution of  $\text{NaHCO}_3$  and NaCl, and then dried over  $\text{MgSO}_4$ . The solvent was removed by evaporation. The residue was purified by silica gel column chromatography ( $\text{CH}_2\text{Cl}_2/\text{MeOH}$ , 20:1) to give a solid yellow product. Other SP-PSt-SP with different molecular weights were also prepared by this process, and the results are shown in Fig. S5. Single-ended SP-functionalized polystyrene ( $\text{PSt}_{70}\text{-SP}$ ) was prepared using the same method.

#### **Synthesis of $\alpha,\omega$ -styrylpyrene-terminated PCL or PEO (SP-PCL-SP or SP-PEO-SP).**

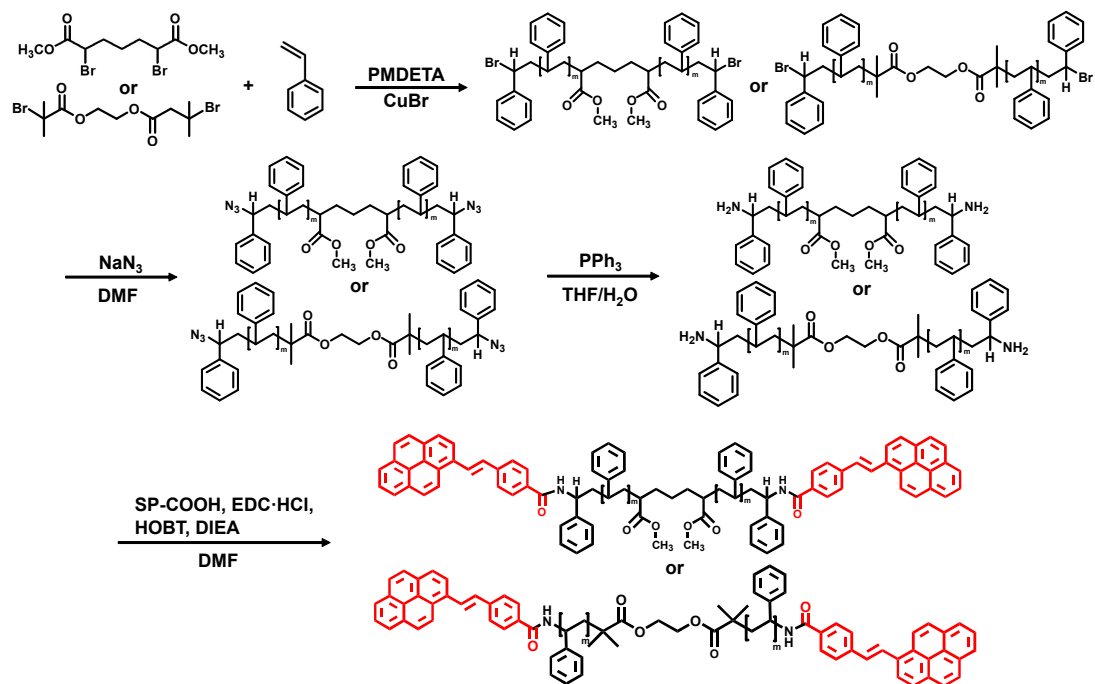
Telechelic polycaprolactone or polyethylene oxide with styrylpyrenyl end groups were synthesized by condensation reaction between hydroxy-terminated polycaprolactone / polyethylene oxide and excessive SP-COOH. The typical experimental process was as follows: SP-COOH (0.14 g, 0.4 mmol, 4 eq), EDC·HCl (0.11 g, 0.6 mmol, 6 eq),

DMAP (0.04 g , 0.3 mmol, 3 eq) and TEA(85  $\mu$ L, 0.6 mmol, 6 eq) were dissolved in 12 mL of DMF and cooled in an ice bath. Then HO-PEO<sub>90</sub>-OH (0.5 g, 0.1 mmol, 1 eq) was added to the reaction mixture, which was stirred at 25 °C for 48 h. The product was diluted with a small amount of EtOAc, and the organic layer was washed with saturated aqueous solution of NaHCO<sub>3</sub> and NaCl, and then dried over MgSO<sub>4</sub>. The solvent was removed by evaporation. The residue was purified by silica gel column chromatography (CH<sub>2</sub>Cl<sub>2</sub>/MeOH, 20:1) to give a solid yellow product . (SP-PEO<sub>90</sub>-SP, 0.40 g, yield 81%).

The SP-PCL-SP series of telechelic polymers, *i.e.* SP-PCL<sub>21</sub>-SP, SP-PCL<sub>38</sub>-SP, and SP-PCL<sub>116</sub>-SP, were synthesized following a similar procedure to give products as yellow solids with yields of 71%, 80%, and 84%, respectively.



**Fig. S1** (a) Synthetic route towards SP-COOH. (b)  $^1\text{H}$  NMR and (c)  $^{13}\text{C}$  NMR spectra of SP-COOH in  $\text{DMSO-}d_6$ .



**Fig. S2** Synthetic route towards SP-PSt-SP.



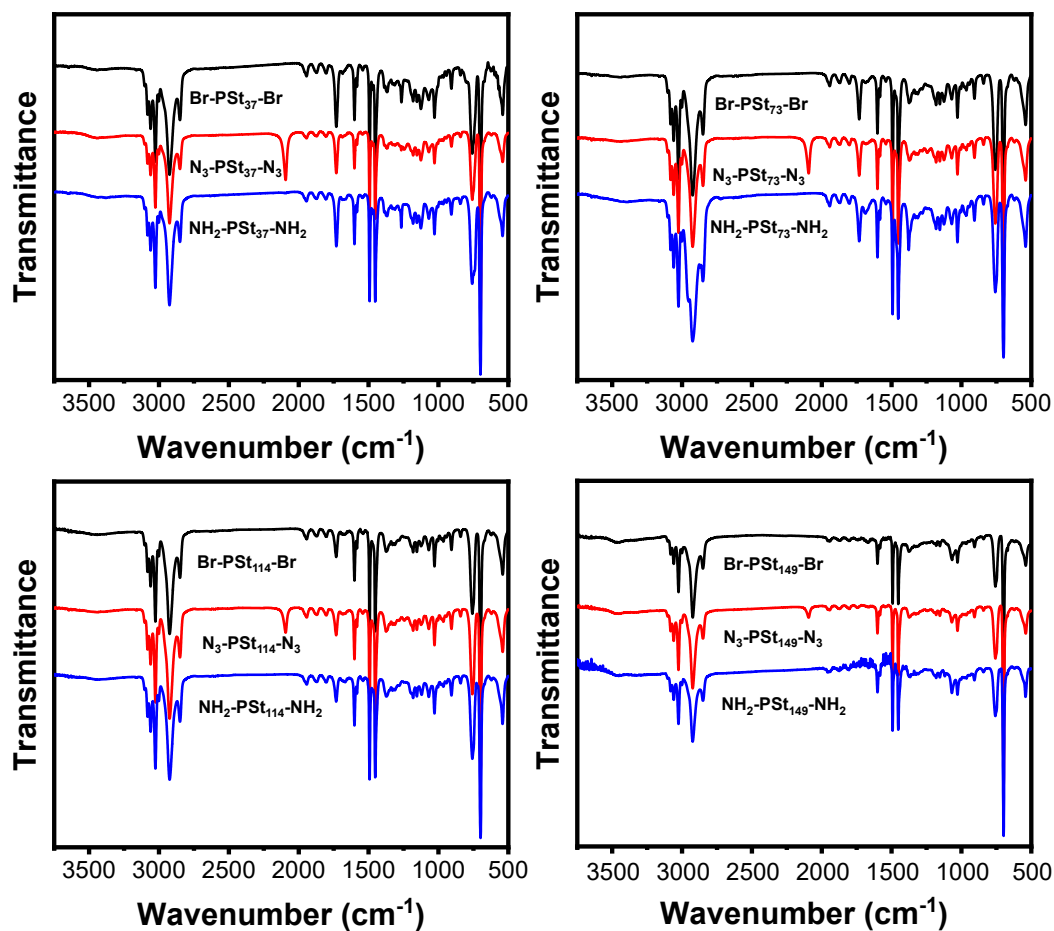
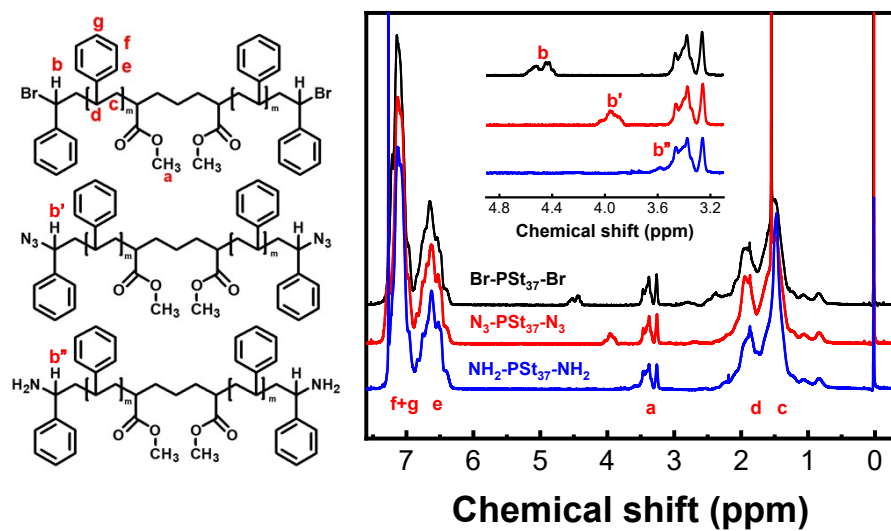


Fig. S3 FT-IR spectra of Br-PSt-Br, N<sub>3</sub>-PSt-N<sub>3</sub>, and NH<sub>2</sub>-PSt-NH<sub>2</sub> with different molecular weights.



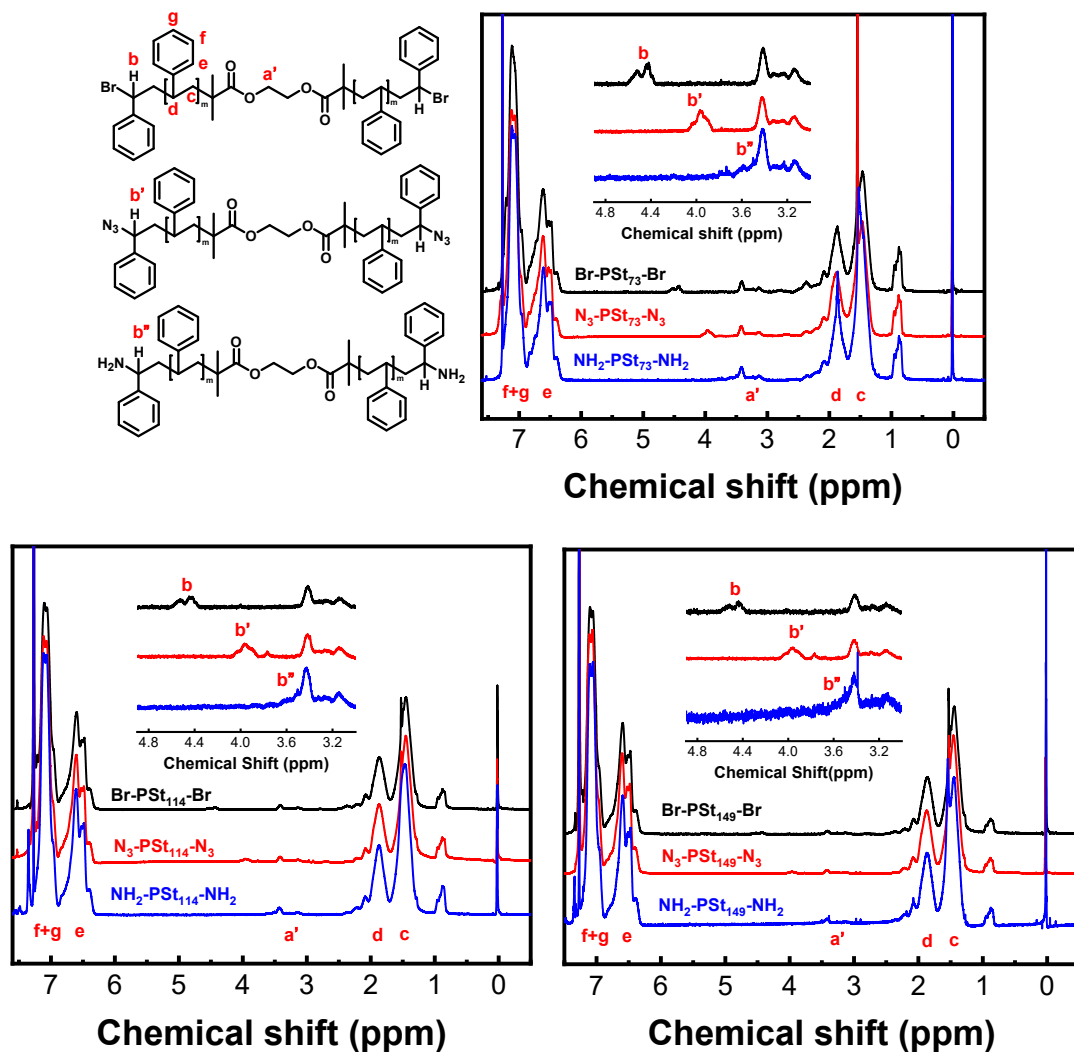
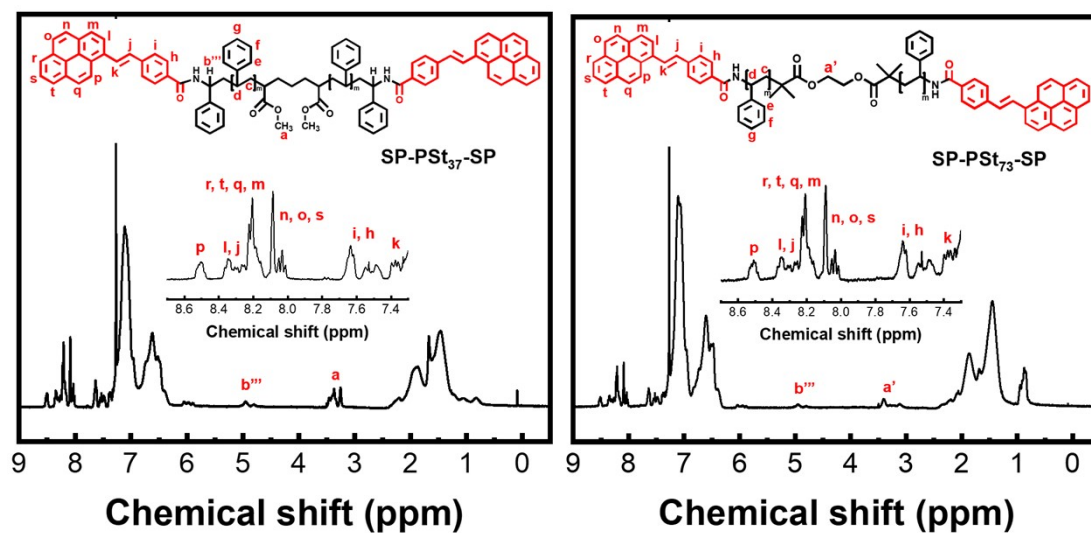
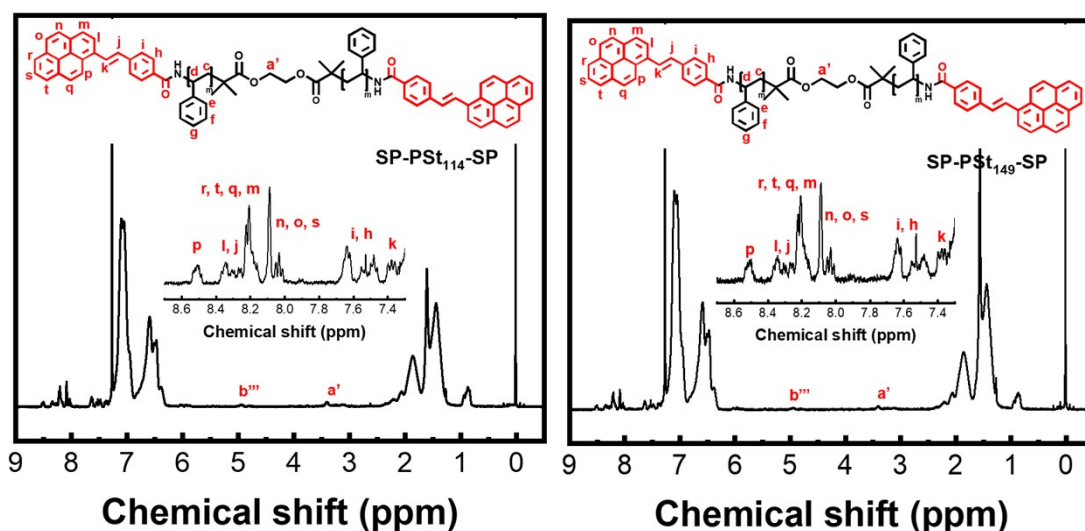
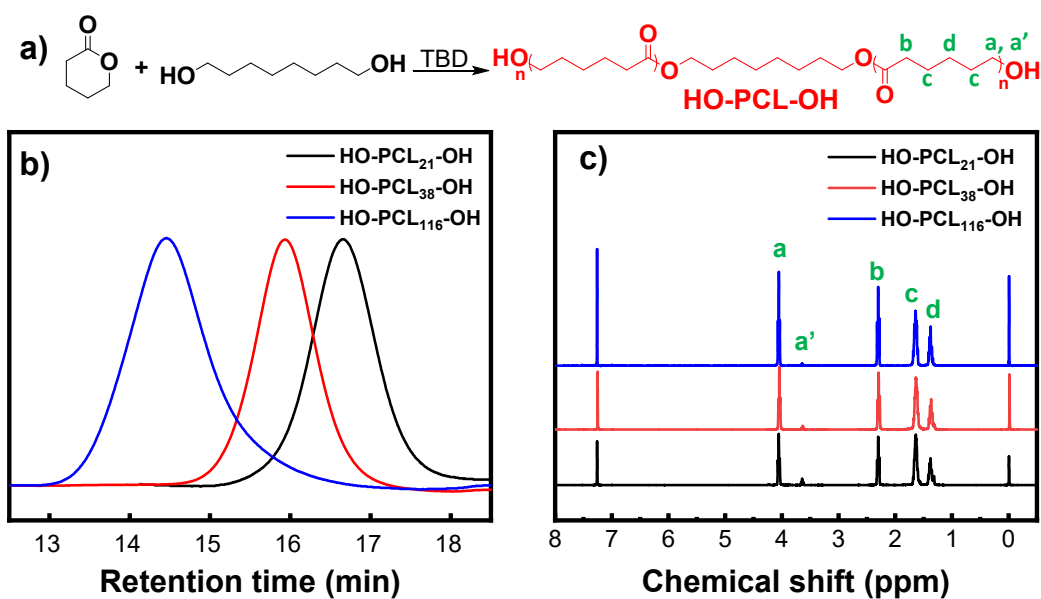


Fig. S4  $^1\text{H}$  NMR spectra of  $\text{Br-PSt-Br}$ ,  $\text{N}_3\text{-PSt-N}_3$ , and  $\text{NH}_2\text{-PSt-NH}_2$  with different molecular weights. The solvent of  $^1\text{H}$  NMR measurements was  $\text{CDCl}_3$

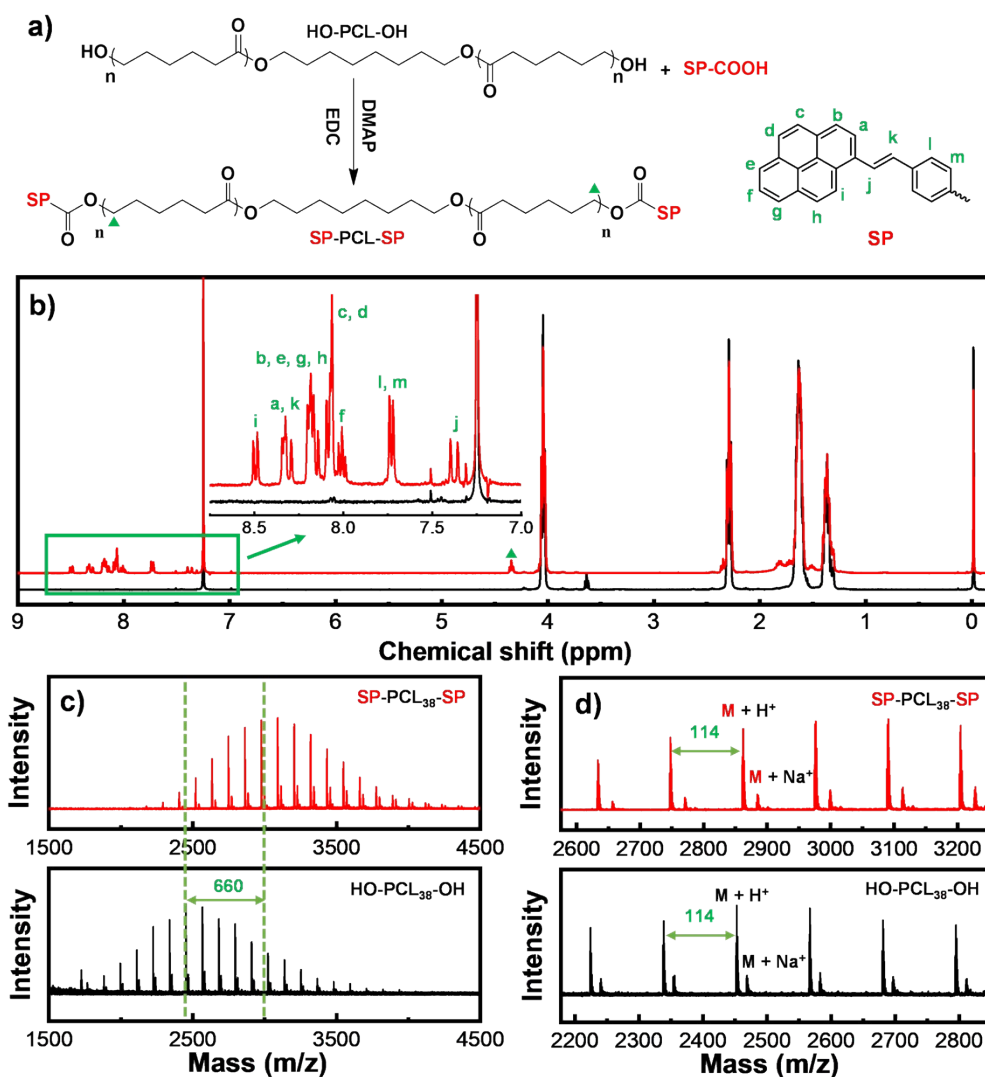




**Fig. S5**  $^1\text{H}$  NMR spectra of SP-PSt-SP with different molecular weights. The solvent of  $^1\text{H}$  NMR measurements was  $\text{CDCl}_3$ .

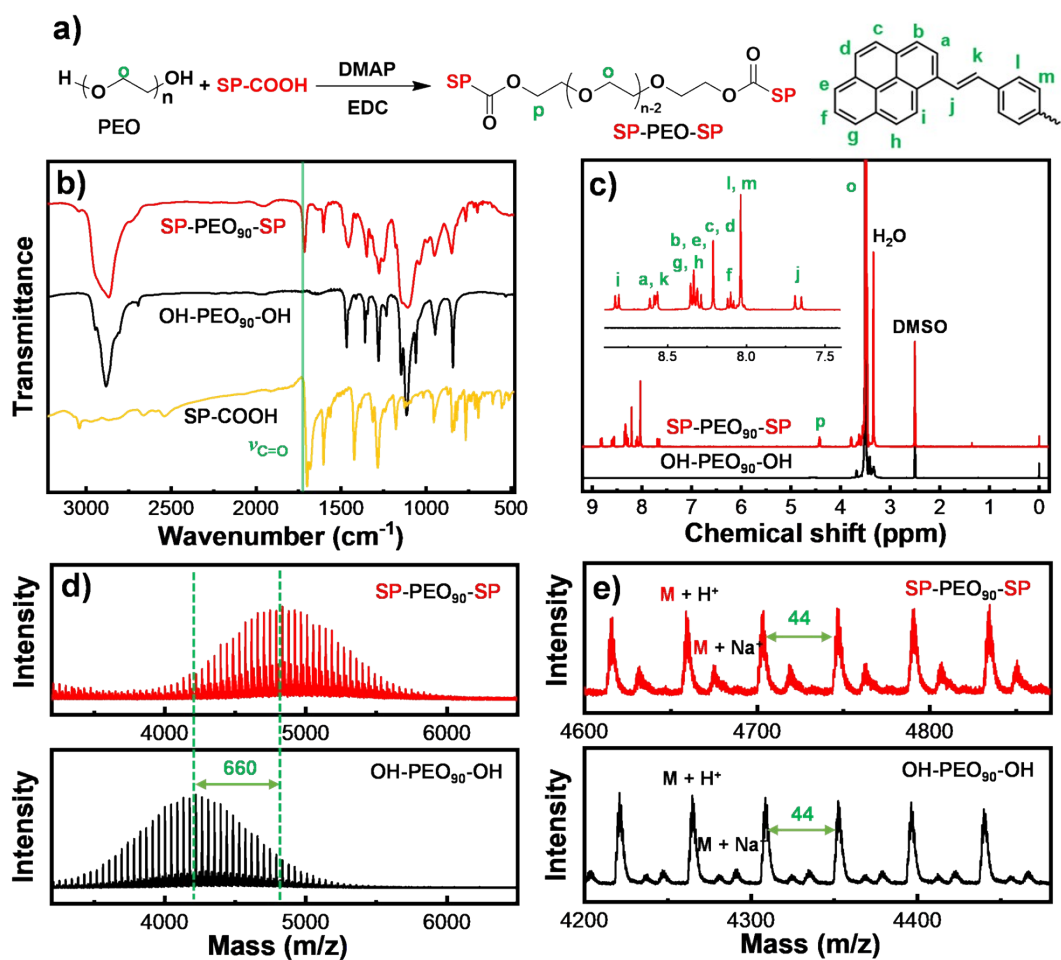


**Fig. S6** (a) Synthetic route towards  $\text{HO-PCL}_n\text{-OH}$  ( $n = 21, 38$  or  $116$ ). (b) SEC elution traces and (c)  $^1\text{H}$  NMR spectra of  $\text{HO-PCL}_n\text{-OH}$ . The solvent of  $^1\text{H}$  NMR measurements was  $\text{CDCl}_3$ .

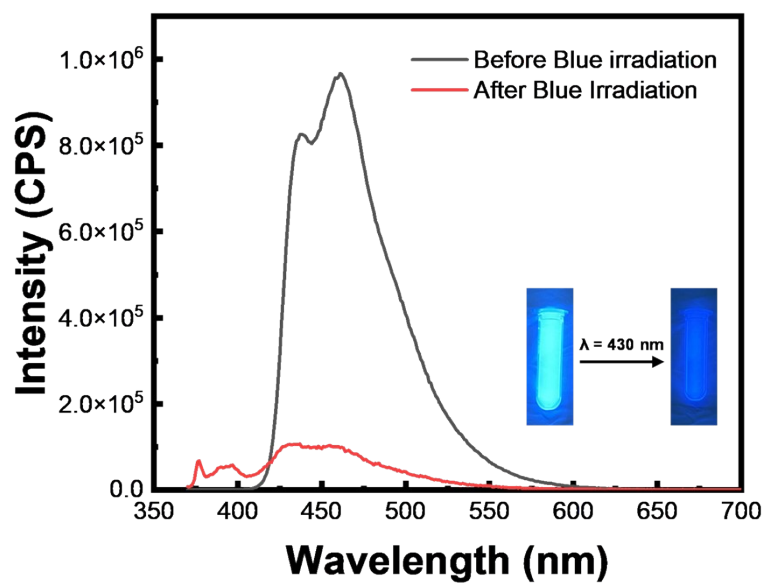


**Fig. S7** (a) Synthetic route towards SP-PCL-SP. (b) <sup>1</sup>H NMR spectra of HO-PCL<sub>38</sub>-OH (black line) and SP-PCL<sub>38</sub>-SP (red line) in CDCl<sub>3</sub>. (c, d) MALDI-TOF mass spectra of HO-PCL<sub>38</sub>-OH (black line) and SP-PCL<sub>38</sub>-SP (red line).

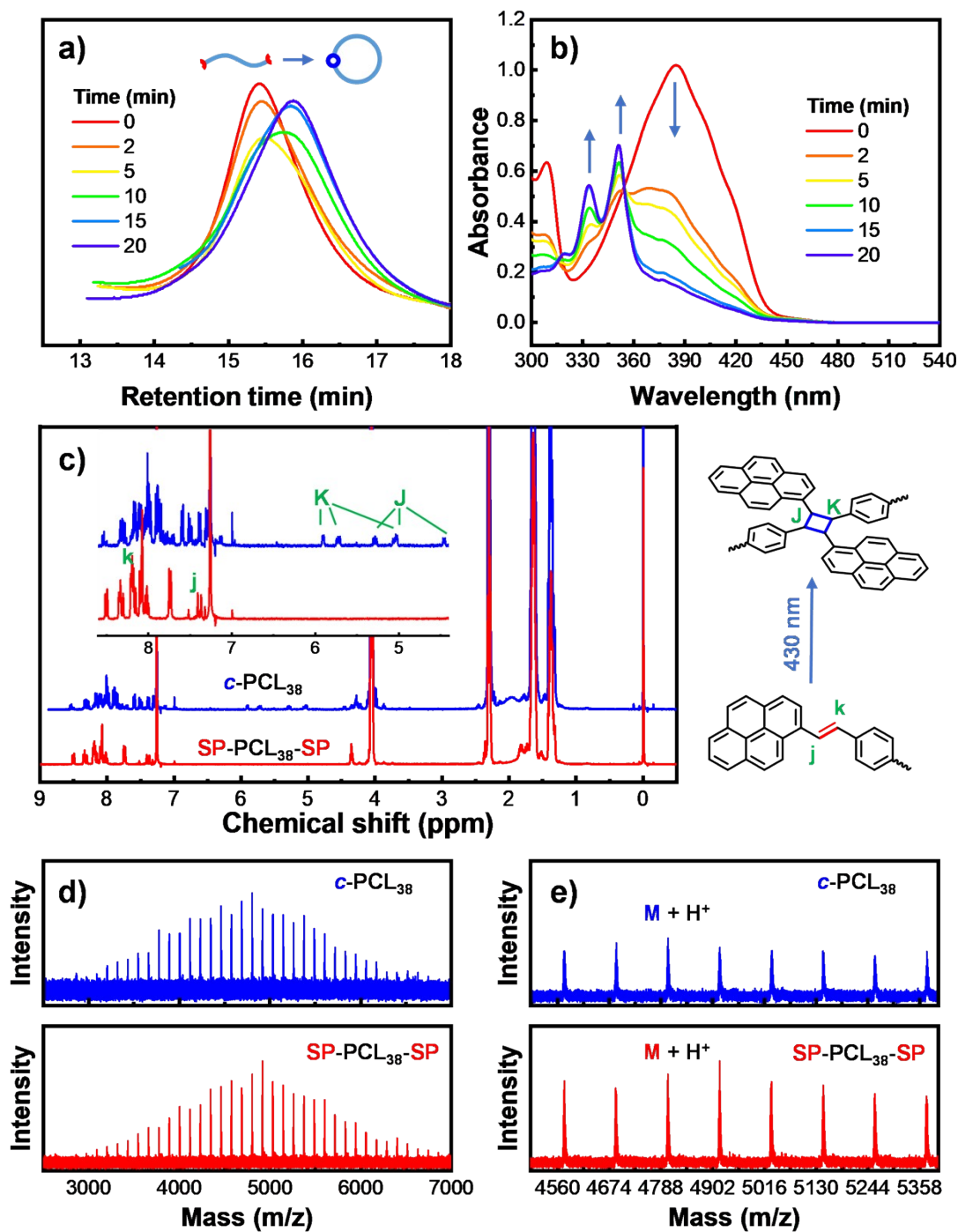
The <sup>1</sup>H NMR spectra (Fig. S7b) of SP-PCL-SP show the peaks of methylene protons adjacent to the ester group at 4.3 ppm (▲) and aromatic protons of SP at 7.0-8.5 ppm (a-m), respectively, indicating that the SP groups were successfully introduced into PCL via ester bond. In addition, MALDI-TOF MS was used to determine the change in molecular weight before and after functionalization, as shown in Figs. S7c and S7d. The resulting spectra exhibit two distinct molecular weights with a mass offset of approximately 660 Da, which is exactly twice the molecular weight of an SP group.



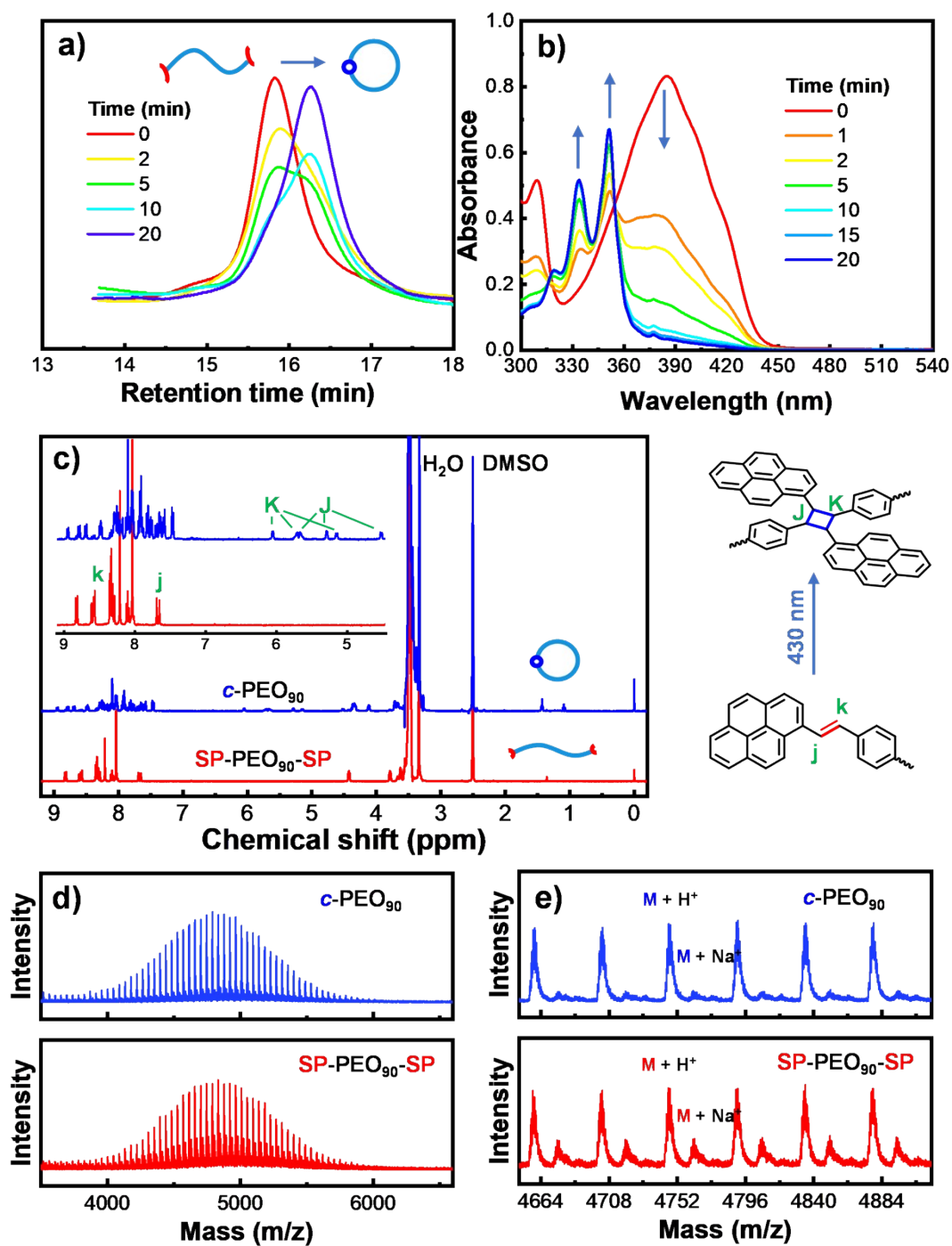
**Fig. S8** (a) Synthetic route towards SP-PEO-SP. (b) FT-IR spectra of SP-COOH, HO-PEO<sub>90</sub>-OH and SP-PEO<sub>90</sub>-SP. (c) <sup>1</sup>H NMR spectra of HO-PEO<sub>90</sub>-OH and SP-PEO<sub>90</sub>-SP in DMSO-*d*<sub>6</sub>. (d, e) MALDI-TOF mass spectra of HO-PEO<sub>90</sub>-OH and SP-PEO<sub>90</sub>-SP.



**Fig. S9** Fluorescence emission spectra of SP-PSt<sub>26</sub>-SP before and after irradiation in THF.  $\lambda_{\text{ex}} = 350$  nm. Insets are the corresponding digital photographs of SP-PSt<sub>26</sub>-SP and *c*-PSt<sub>26</sub> under UV light ( $\lambda = 365$  nm).

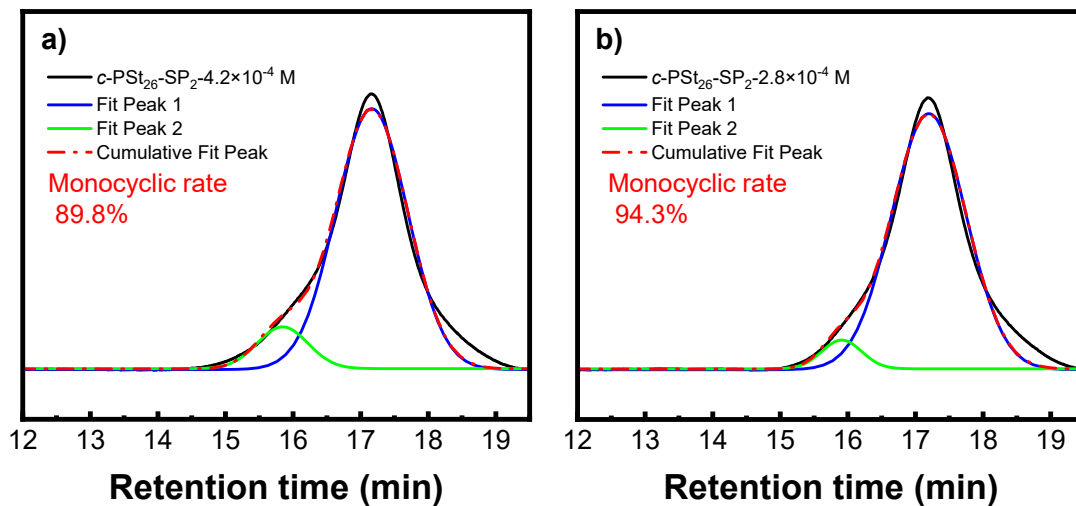


**Fig. S10** (a) SEC elution traces and (b) the corresponding UV-vis spectra of SP-PCL<sub>38</sub>-SP before and after irradiation at 430 nm in THF for different times. (c) <sup>1</sup>H NMR and (d, e) MALDI-TOF mass spectra of SP-PCL<sub>38</sub>-SP before and after irradiation at 430 nm in THF. The concentration of cyclization was  $5 \times 10^{-5}$  M.

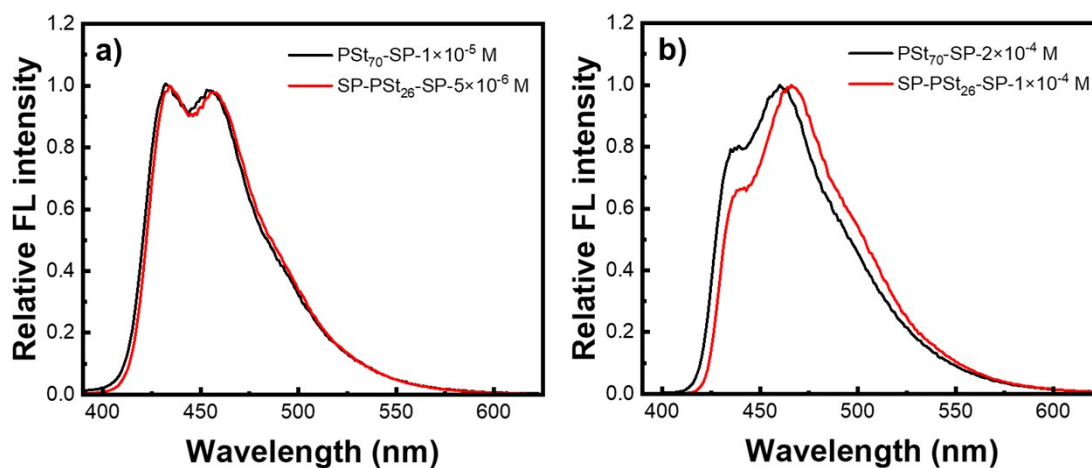


**Fig. S11** (a) SEC elution traces and (b) UV-vis spectra of SP-PEO<sub>90</sub>-SP before and after irradiation at 430 nm in THF for different times. (c) <sup>1</sup>H NMR and (d, e) MALDI-TOF mass spectra of SP-PEO<sub>90</sub>-SP before and after irradiation at 430 nm in THF. The concentration of cyclization was  $5 \times 10^{-5}$  M.

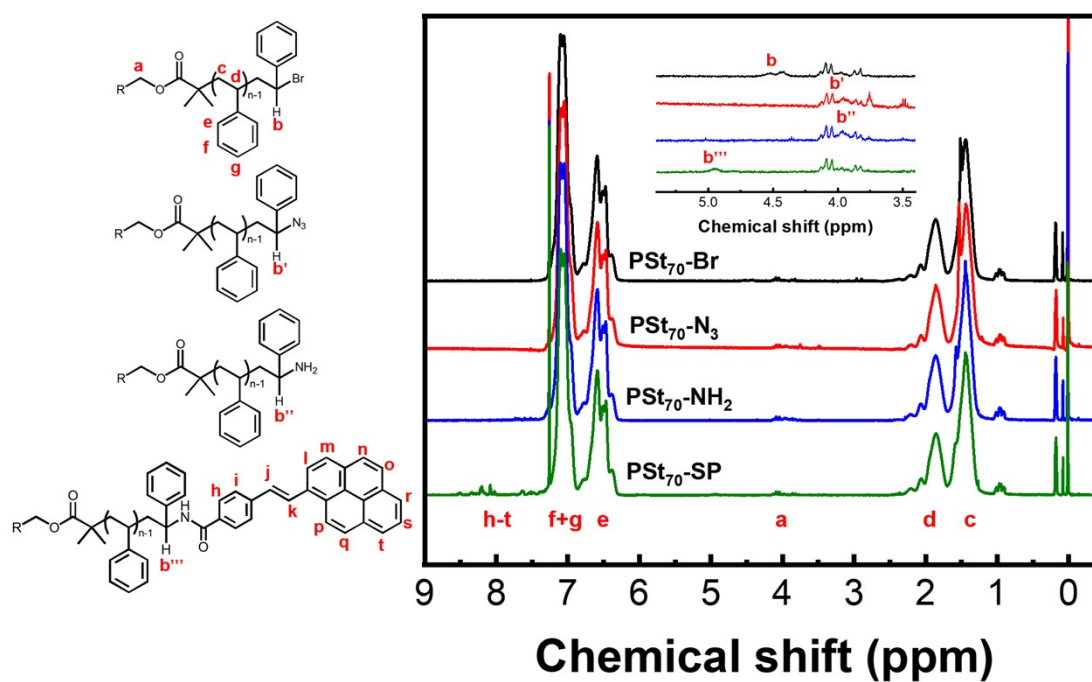




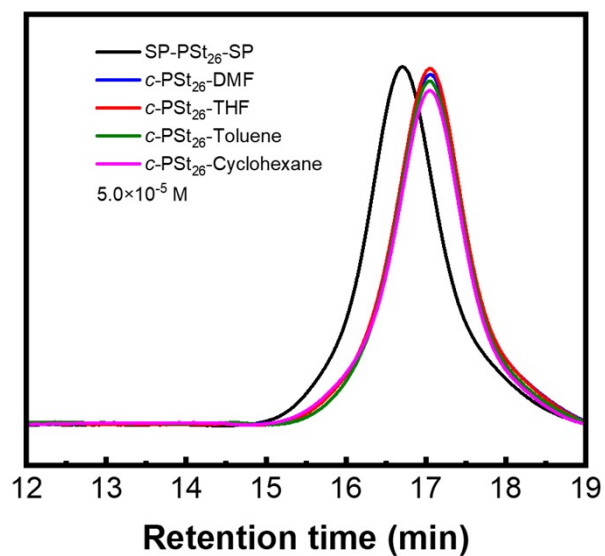
**Fig. S12** Peak splitting of the SEC curve of the cyclization products before and after irradiation at 430 nm with different concentrations in THF using Gaussian function peak fitting. The black curves are the original SEC elution traces.



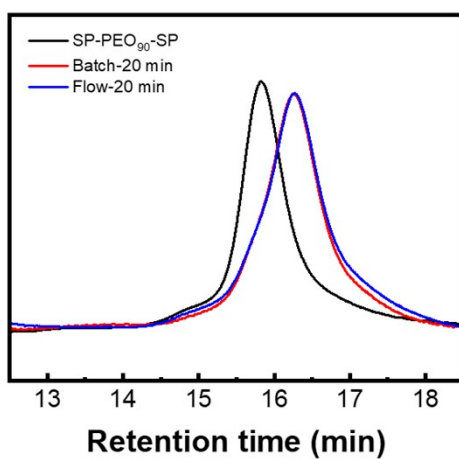
**Fig. S13** Fluorescence emission spectra of PSt<sub>70</sub>-SP and SP-PSt<sub>26</sub>-SP with different concentrations in THF.  $\lambda_{\text{ex}} = 350$  nm.



**Fig. S14** <sup>1</sup>H NMR spectra of PSt<sub>70</sub>-Br (black line), PSt<sub>70</sub>-N<sub>3</sub> (red line), PSt<sub>70</sub>-NH<sub>2</sub> (blue line), PSt<sub>70</sub>-SP (green line), respectively. The solvent of <sup>1</sup>H NMR measurements was CDCl<sub>3</sub>.

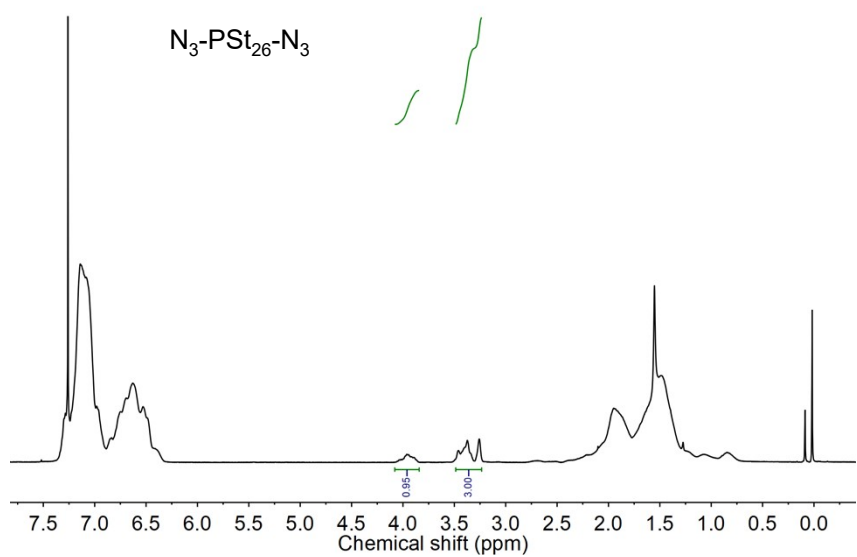
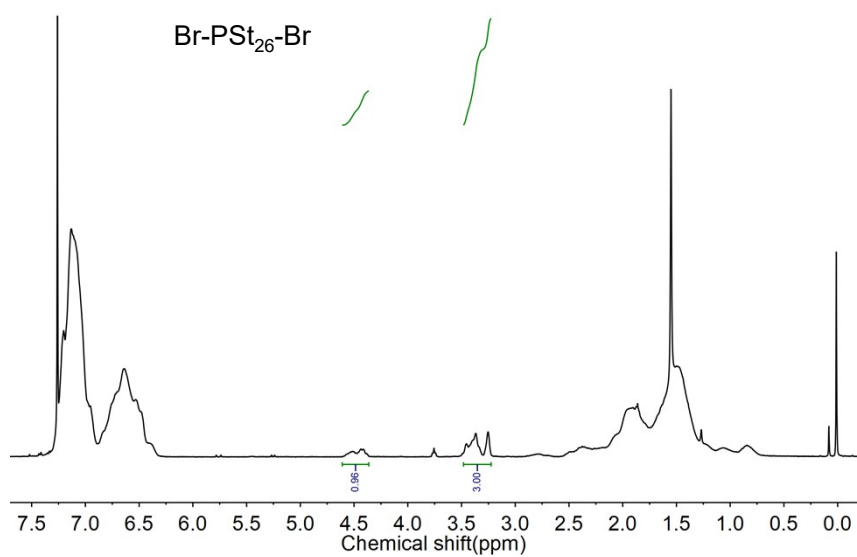


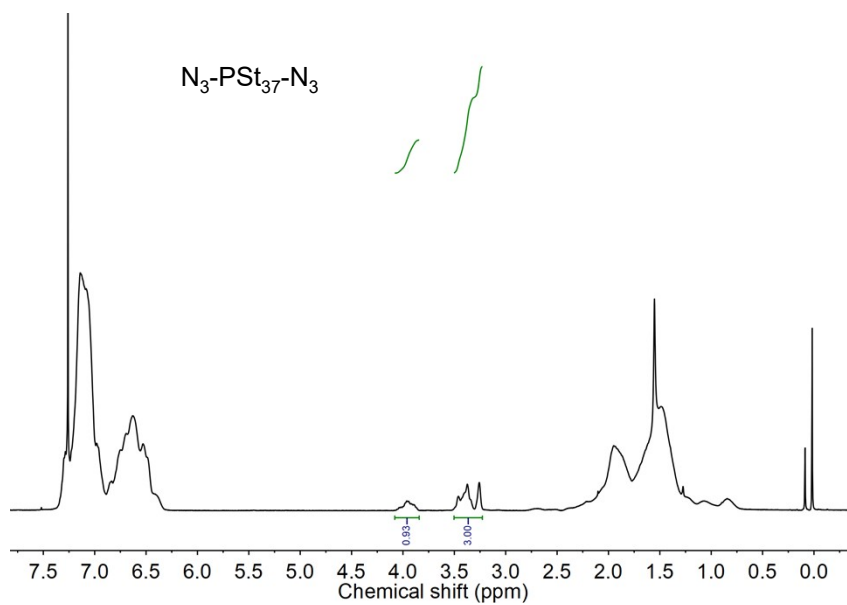
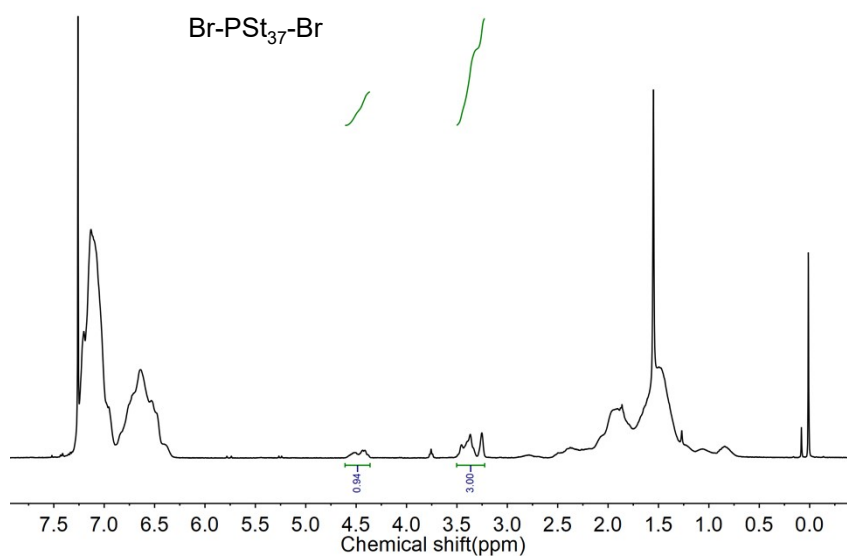
**Fig. S15** SEC elution traces of SP-PSt<sub>26</sub>-SP before and after photoirradiation in different solvents.

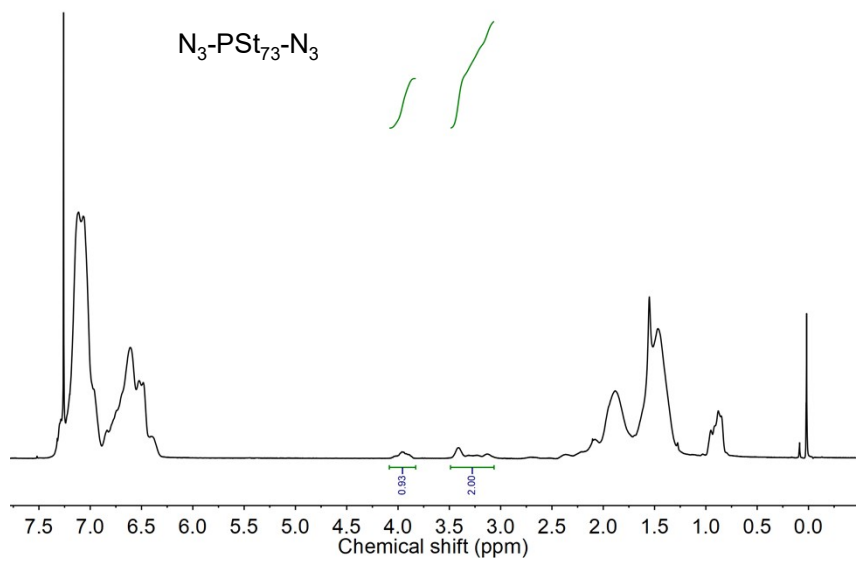
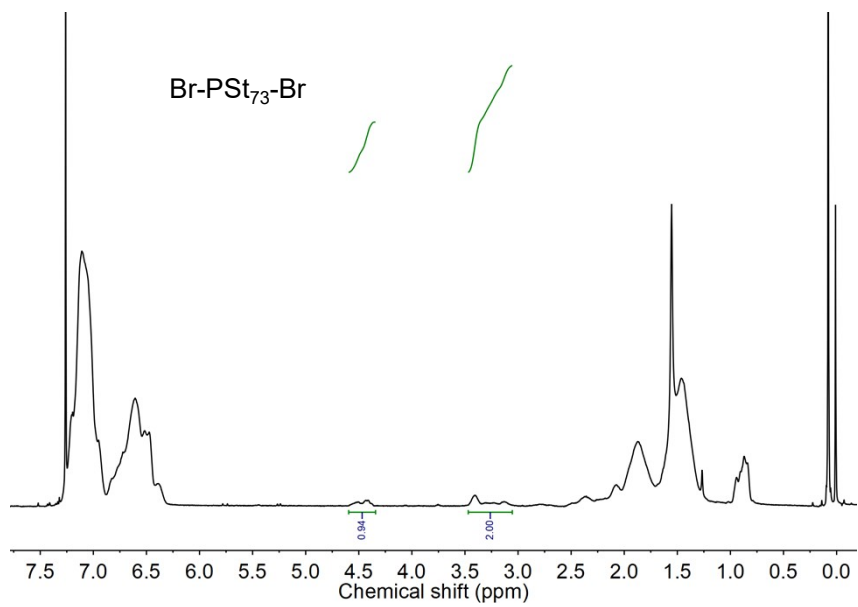


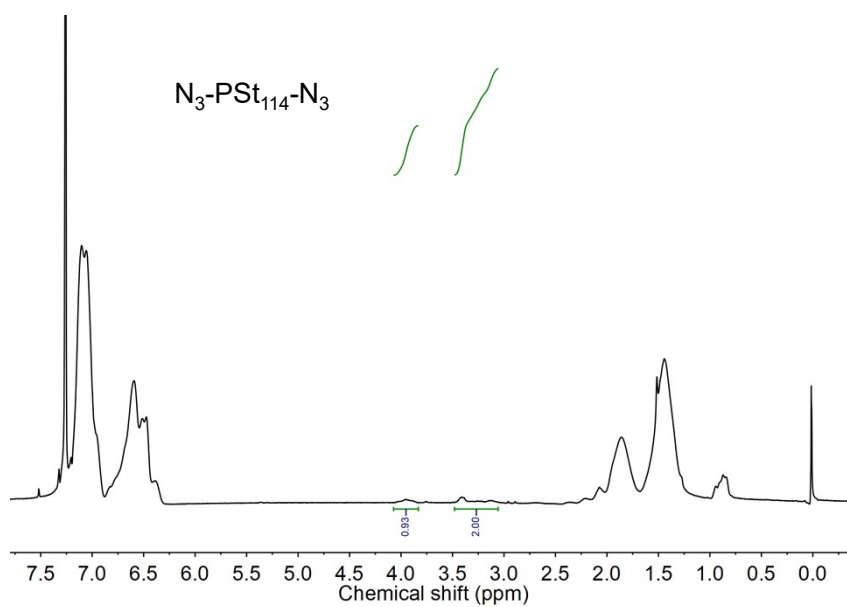
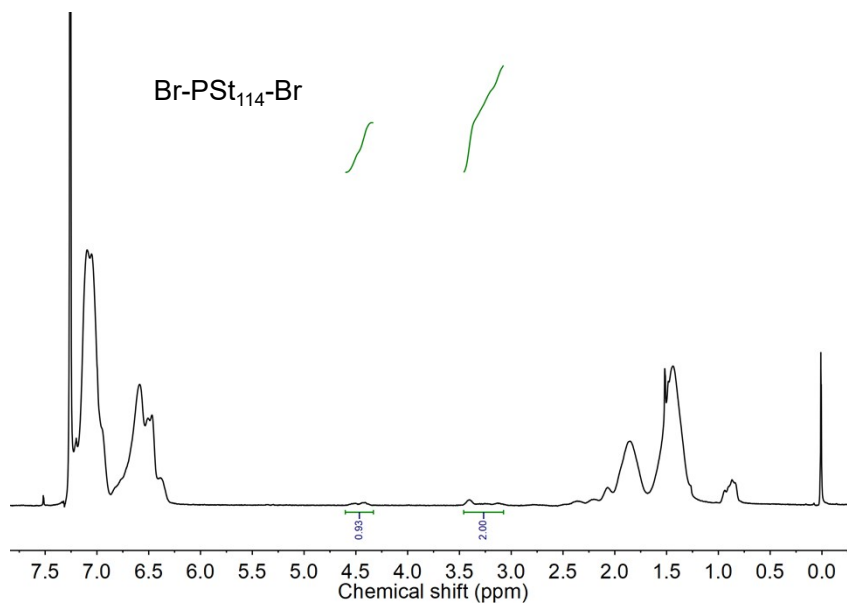
**Fig. S16** SEC elution traces of SP-PEO<sub>90</sub>-SP before and after photoirradiation in batch and continuous-flow reactor.

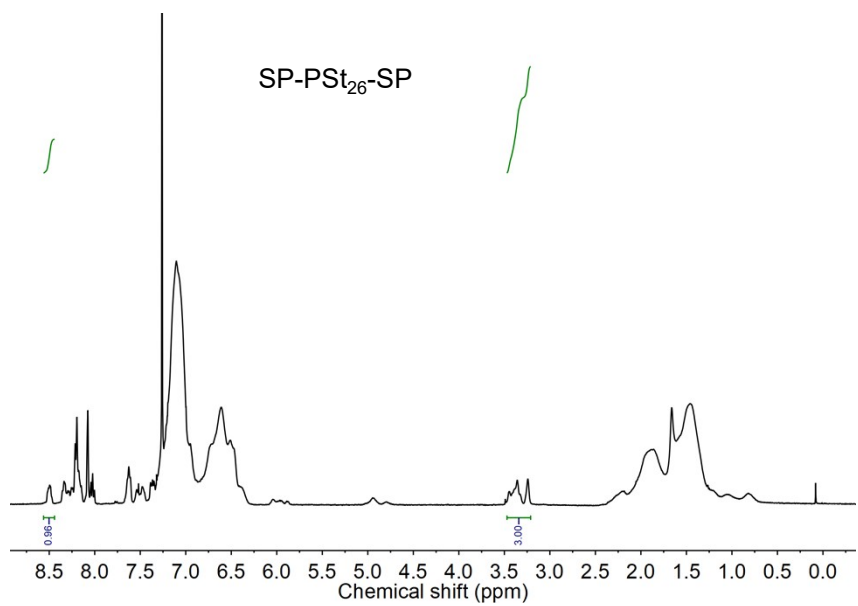
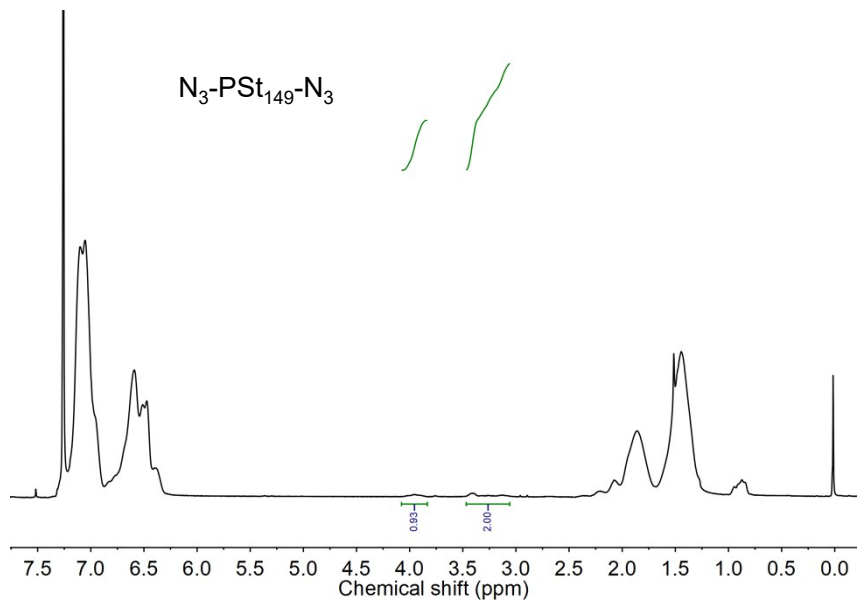
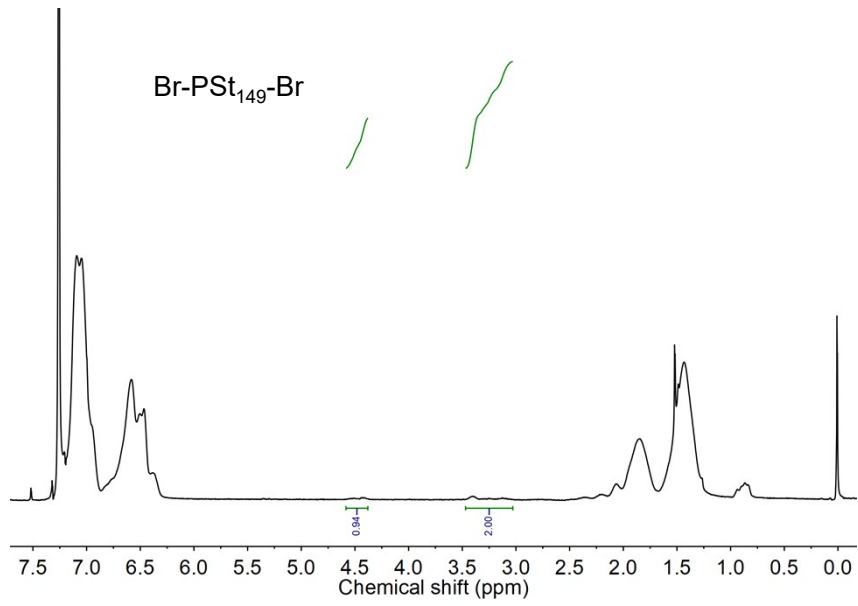
The  $^1\text{H}$  NMR integral spectra of Br-PSt<sub>26</sub>-Br, N<sub>3</sub>-PSt<sub>26</sub>-N<sub>3</sub>, and SP-PSt-SP:



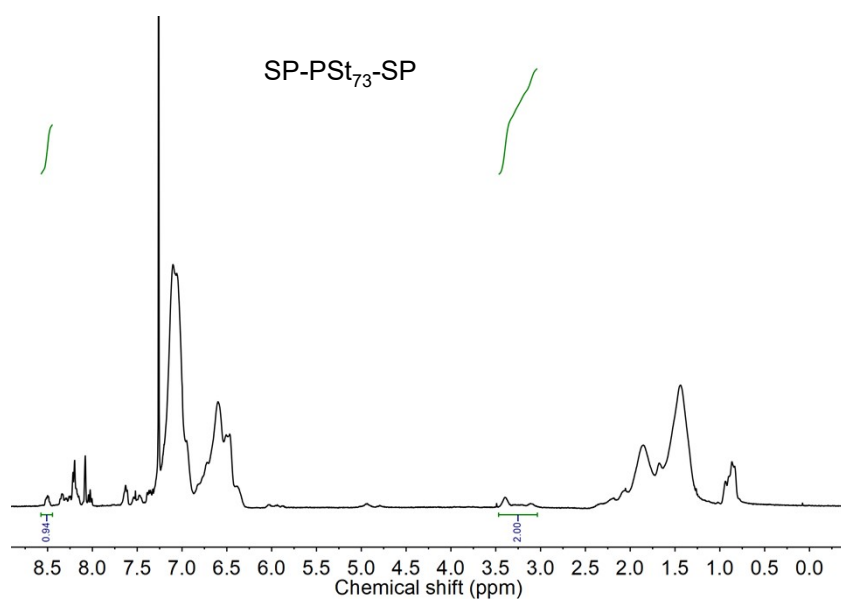
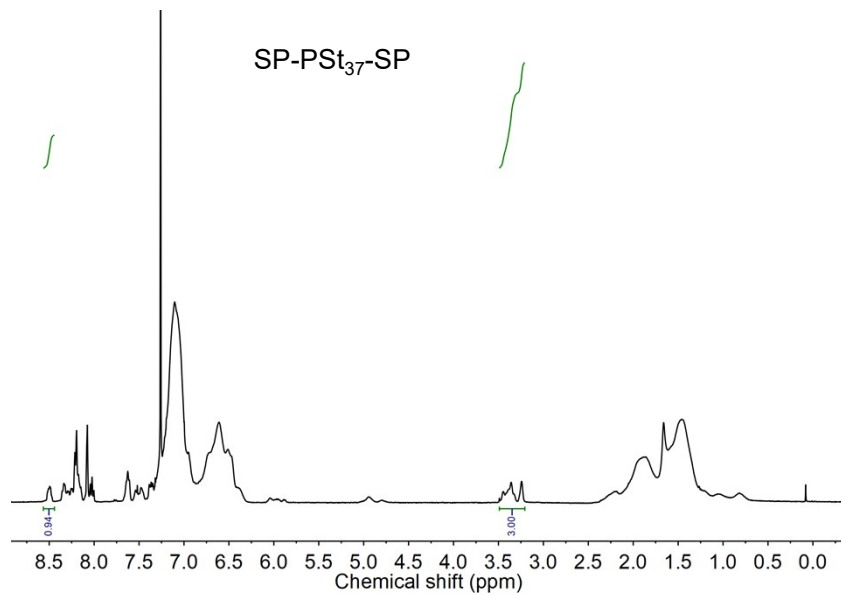


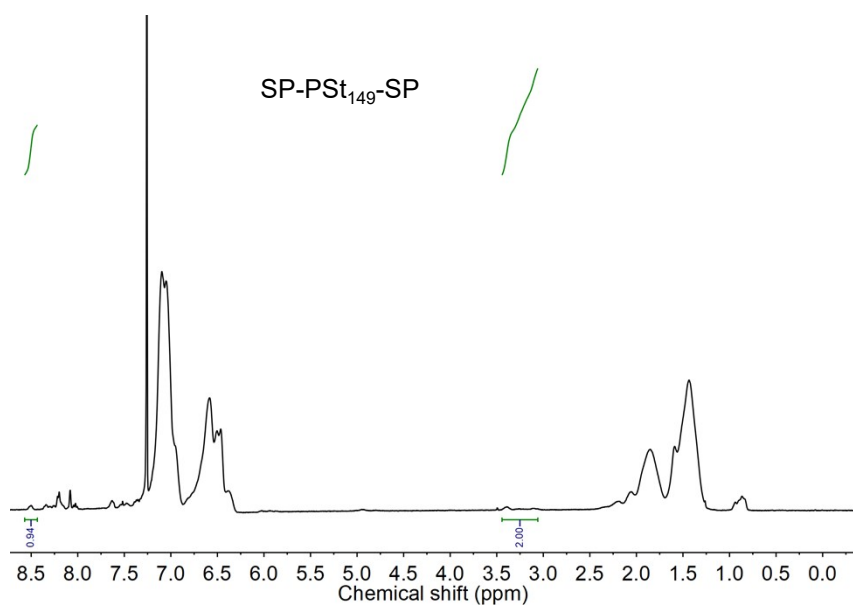
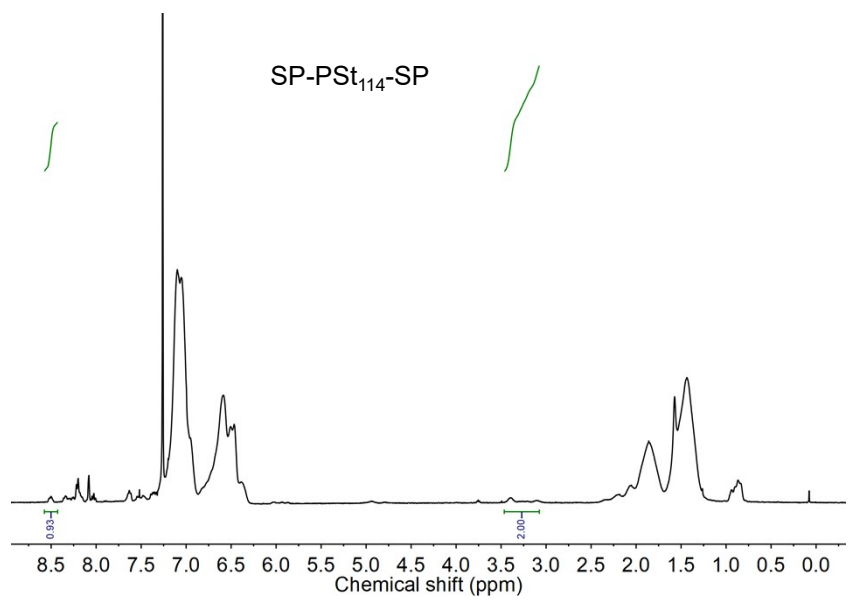












**Table S1.** Mass determination of polystyrene with different end groups (R-PSt-R).

Sample	R= Br			R= N <sub>3</sub>			R= NH <sub>2</sub>			R= SP		
	Mn (g/mol)	PDI	Conversion (%)	Mn (g/mol)	PDI	Conversion (%)	Mn (g/mol)	PDI	Conversion (%)	Mn (g/mol)	PDI	Conversion (%)
R-PSt <sub>26</sub> -R	2900	1.12	30	2980	1.12	95	2960	1.12	60	3540	1.12	81
R-PSt <sub>37</sub> -R	4200	1.13	21	4300	1.13	89	4210	1.13	42	4790	1.13	69
R-PSt <sub>73</sub> -R	8000	1.14	28	7960	1.14	91	8040	1.15	50	8670	1.15	71
R-PSt <sub>114</sub> -R	11800	1.13	18	12000	1.13	93	12010	1.14	52	12500	1.14	79
R-PSt <sub>149</sub> -R	15000	1.22	19	14920	1.22	92	14980	1.22	55	15600	1.22	75

**Table S2.** Mass determination of HO-PCL<sub>n</sub>-OH by SEC and <sup>1</sup>H NMR.

Sample	$M_{n, SEC}^a$	PDI <sup>a</sup>	$M_n^b$	$M_{n, ^1H NMR}^c$
HO-PCL <sub>21</sub> -OH	5000	1.12	2400	2400
HO-PCL <sub>38</sub> -OH	8800	1.11	4400	4300
HO-PCL <sub>116</sub> -OH	24600	1.19	13300	13200

<sup>a</sup> Calibrated based upon linear polystyrene standards.

<sup>b</sup> Corrected value for PCL using  $M_n(\text{PCL}) = 0.259 \times M_n(\text{PS})^{1.073}$ .

<sup>c</sup> Calculated based upon <sup>1</sup>H NMR, *i.e.*  $M_{n, ^1H NMR} = A_b/A_a \times 2 \times M_{\epsilon\text{-CL}} + M_{1,8\text{-octanediol}}$ .