Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Synthesis and Characterization of Amphiphilic Miktoarm Star Polymers Based on Sydnone-Maleimide Double Cycloaddition

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Synthesis of furan-*N*-propargylmaleimide (7). A three-necked flask was charged with a mixture of maleimide 5.0 g (51.5 mmol) and diethyl ether 100 mL, and then furan 10.51 g (154.5 mmol) was added to the solution whilst stirring. The mixture was stirred at 95 °C for about 12 h under nitrogen. After removing the solvent under reduced pressure, the crude product was purified by silica gel chromatography to give the furan-maleimide 7.51 g. The obtained furan-maleimide (**FM**) 4.13 g (25.0 mmol) was dissolved in dried DMF 50 mL, and then propargyl bromide 8.85 g (75.0 mmol) and K_2CO_3 3.45 g (25.0 mmol) were added to the solution. The mixture was stirred at 65 °C for 12 h under nitrogen. The insoluble powder was filtered and the solvent was removed under reduced pressure. The crude product was purified by silica gel chromatography to give the **furan-*N*-propargylmaleimide** (**7**) 4.61 g, 91 % yield. ^{1}H NMR (500MHz, $CDCl_3$, δ, ppm): 6.55 (t, J=0.9 Hz, 2H, C***H***=C**H**), 5.33 (t, *J*=0.9 Hz, 2H, C***H***OC***H***), 4.26 (d, *J*=2.5 Hz, 2H, NC***H***$_2$C), 2.93 (s, 2H, COC***H***(CH)C***H***(CH)CO), 2.22 (s, 1H, CC***H***).

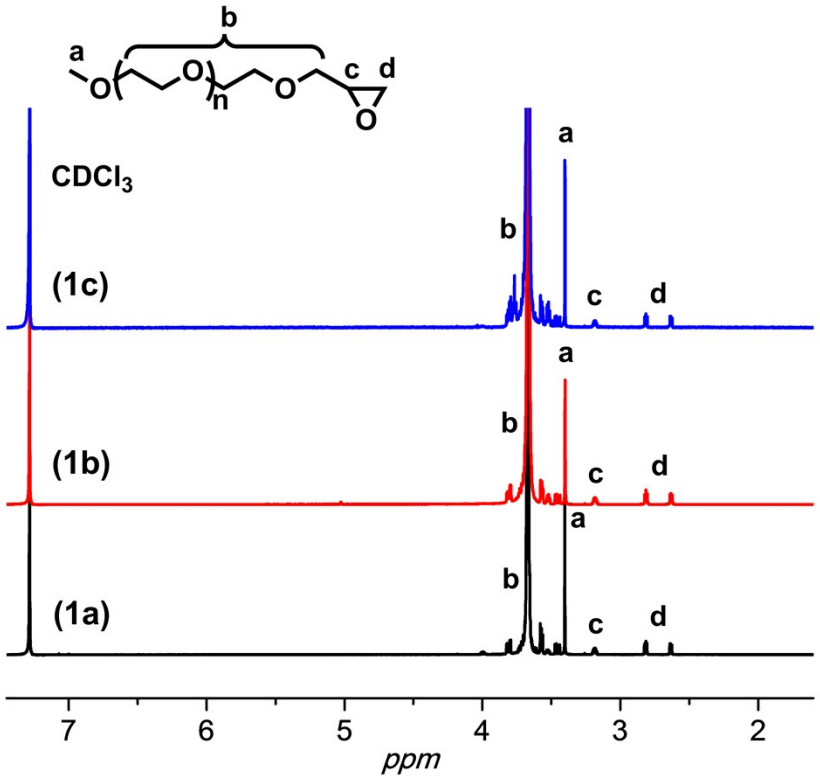

Fig. S1 ^{1}H NMR spectra of **MPEG$_{1k}$-*epoxide*** (**1a-1c**) in $CDCl_3$.

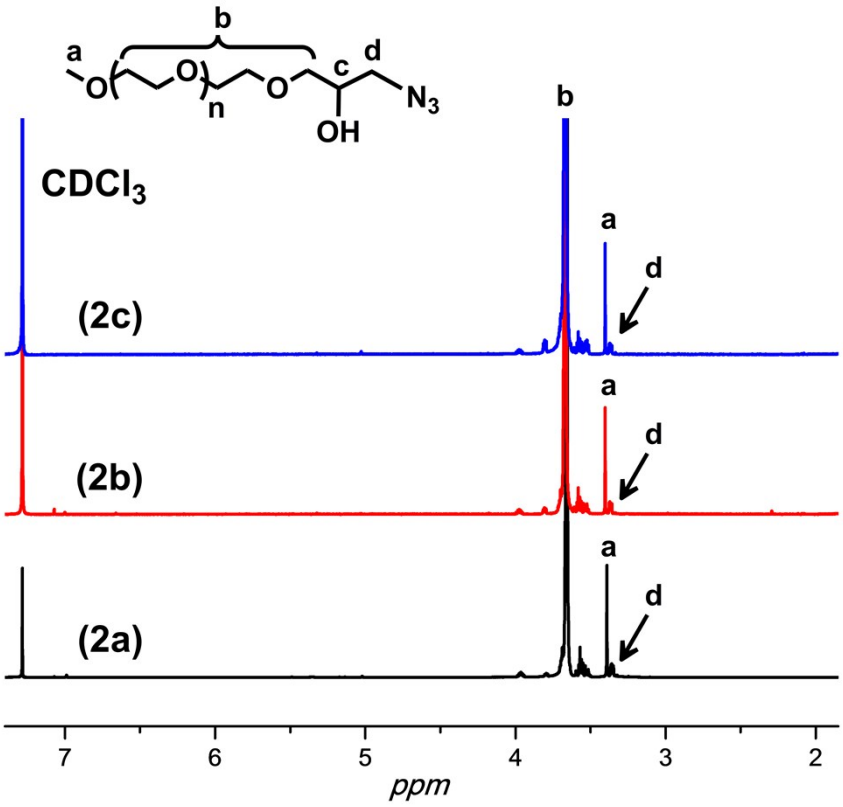

Fig. S2 ^{1}H NMR spectra of **MPEG-(*OH*)(*N*$_3$)** (**2a-2c**) in $CDCl_3$.

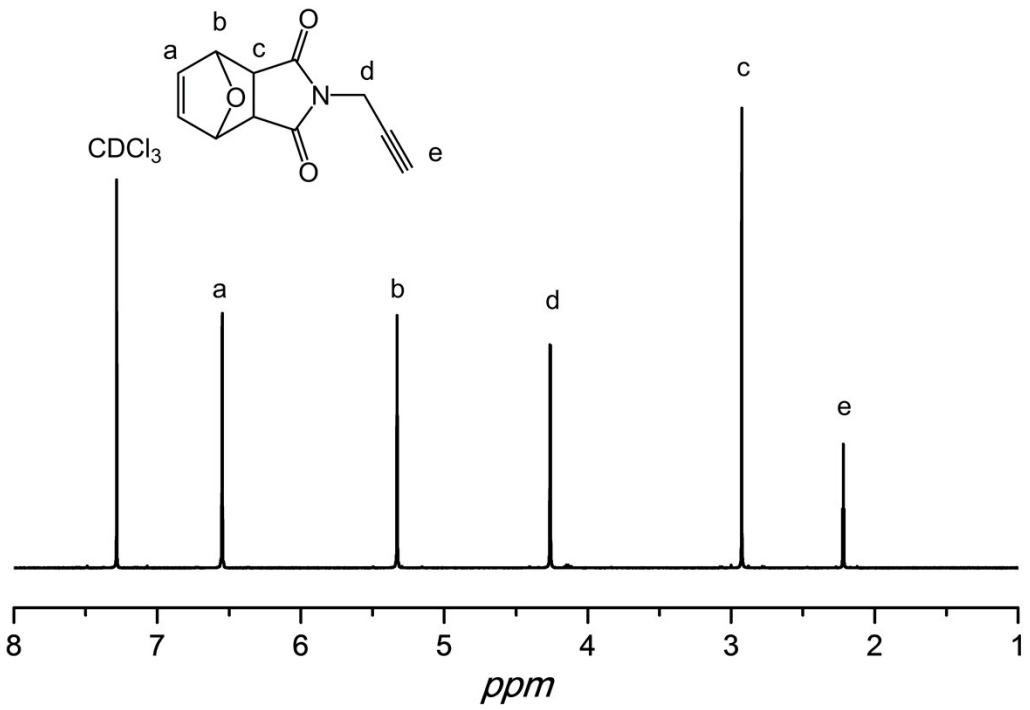

Fig. S3 ^{1}H NMR spectrum of **furan-*N*-propargylmaleimide (7)** in $CDCl_3$.

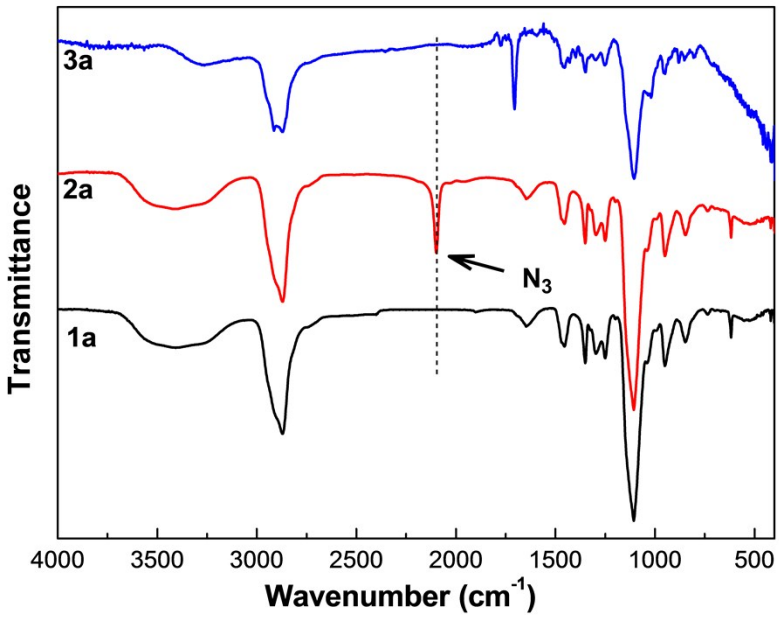

Fig. S4 IR spectra of **1a, 2a** and **3a**.

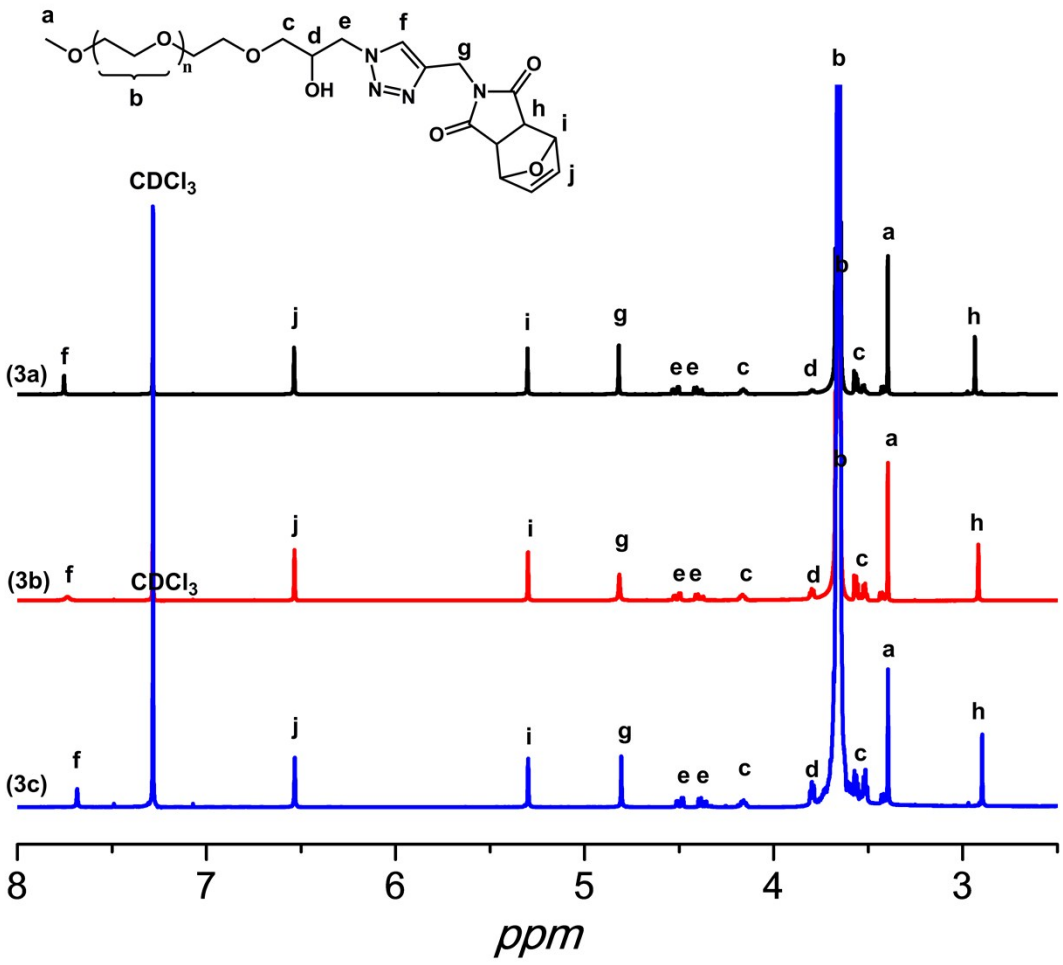

Fig. S5 ^{1}H NMR spectra of **MPEG-(*OH*)(*FM*) (3a-3c)** in $CDCl_3$.

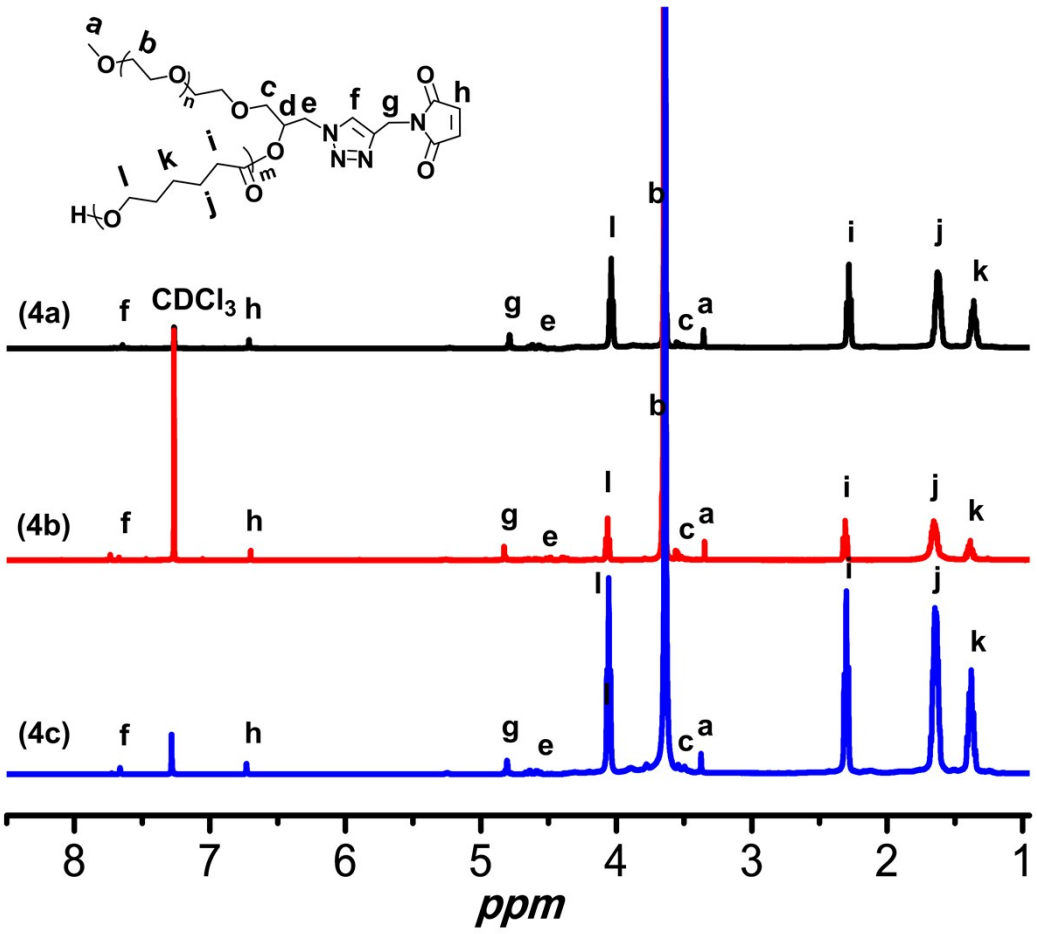

Fig. S6 ^{1}H NMR spectra of **MPEG-*b*-PCL(*MI*) (4a-4c)** in $CDCl_3$.

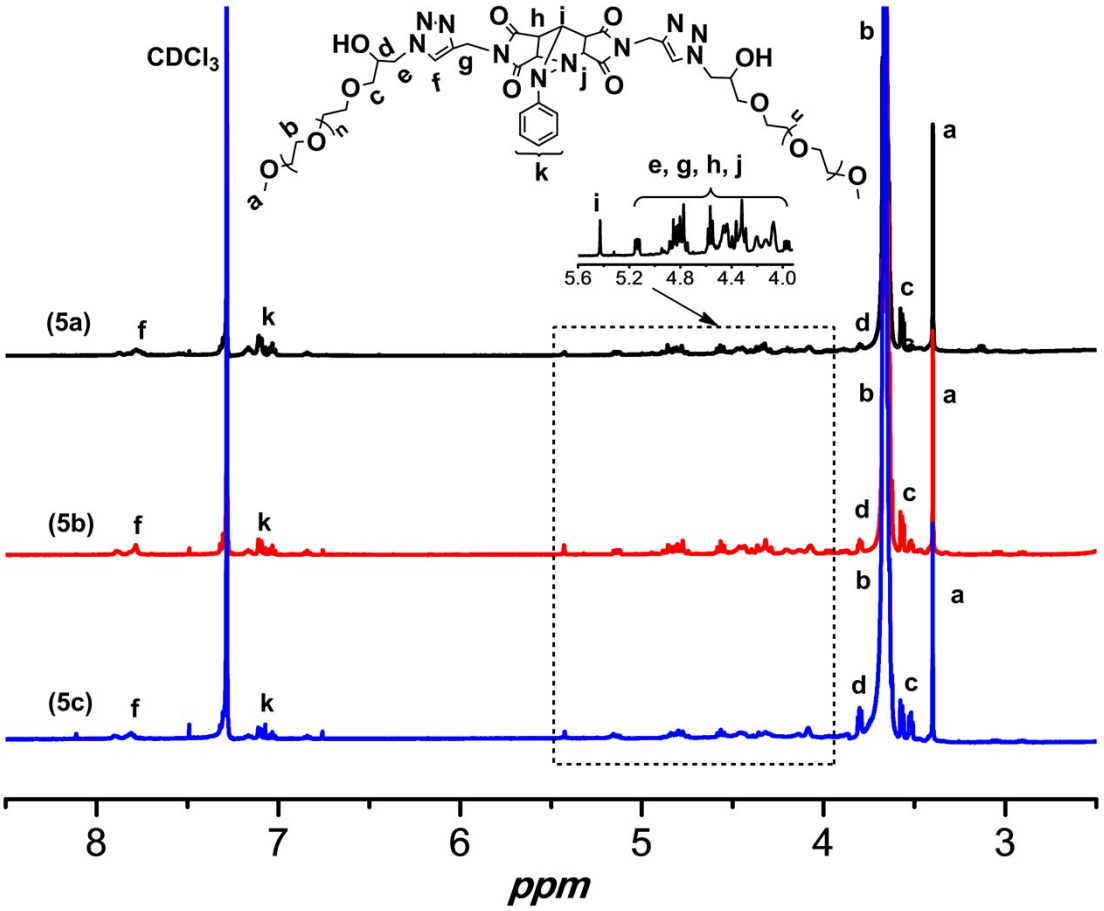

Fig. S7 ^{1}H NMR spectra of **$(MPEG)_2(OH)_2$ (5a-5c)** in $CDCl_3$.

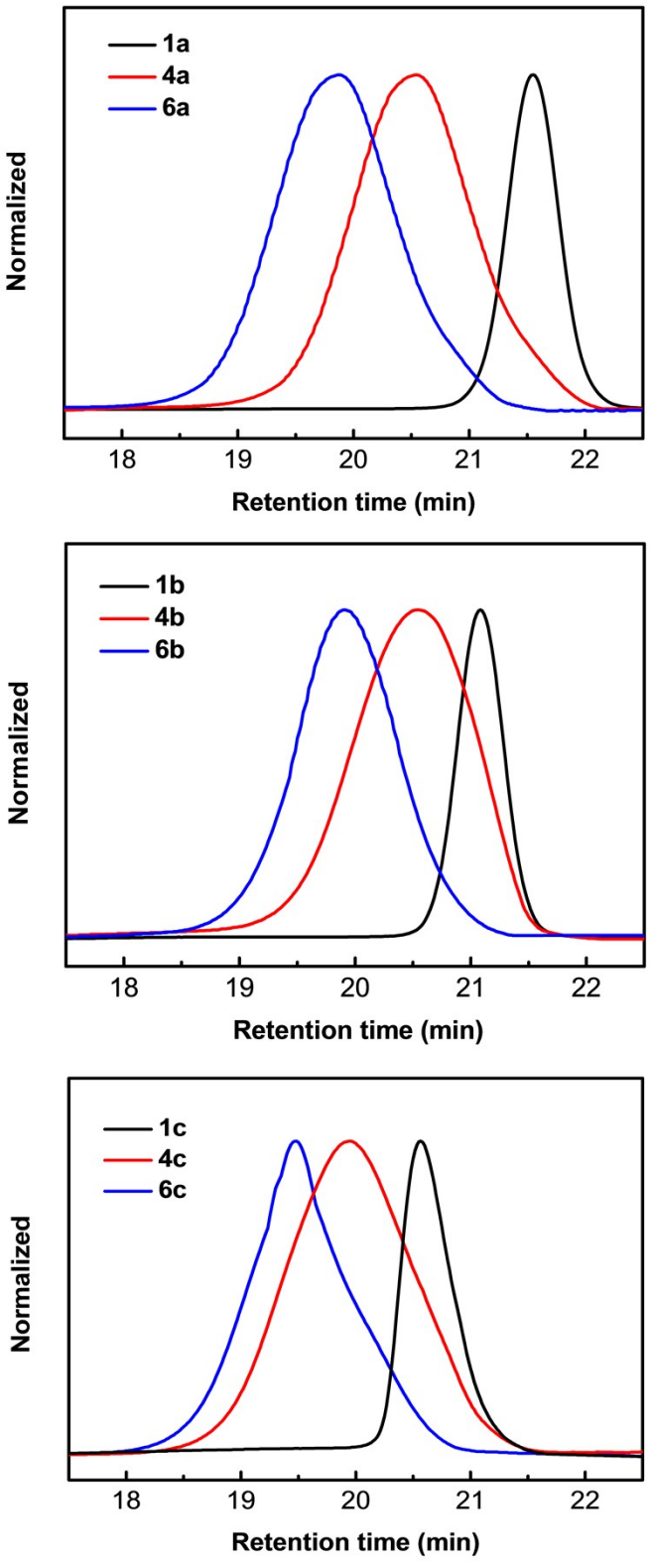

Fig. S8 GPC traces of **$MPEG_{1k}$-*epoxide* (1a-1c)**, **MPEG-*b*-PCL(*MI*) (4a-4c)** and **$(MPEG)_2(PCL)_2$ (6a-6c)** prepared by the "Coupling-onto" approach.

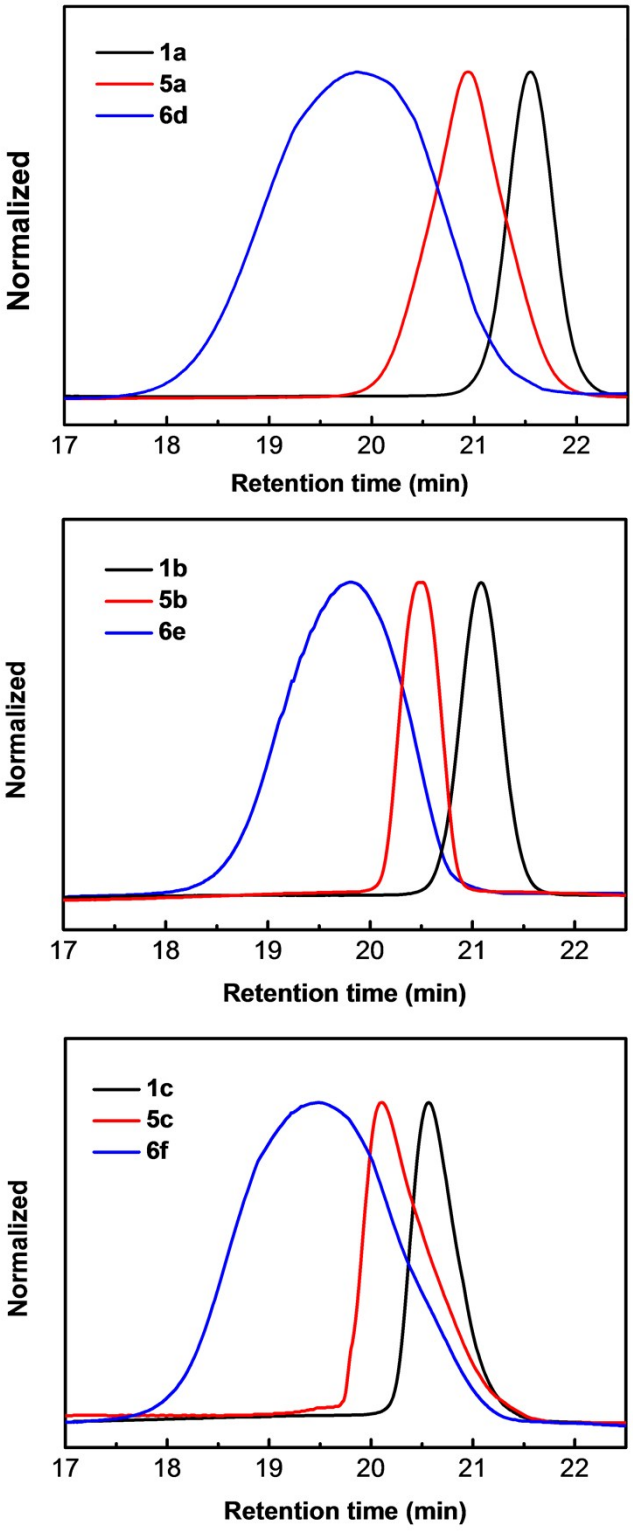

Fig. S9 GPC traces of **$MPEG_{1k}$-*epoxide*** (**1a-1c**), **$(MPEG)_2(OH)_2$** **(5a-5c)** and **$(MPEG)_2(PCL)_2$** (**6d-6f**) prepared by the "In-out" approach.

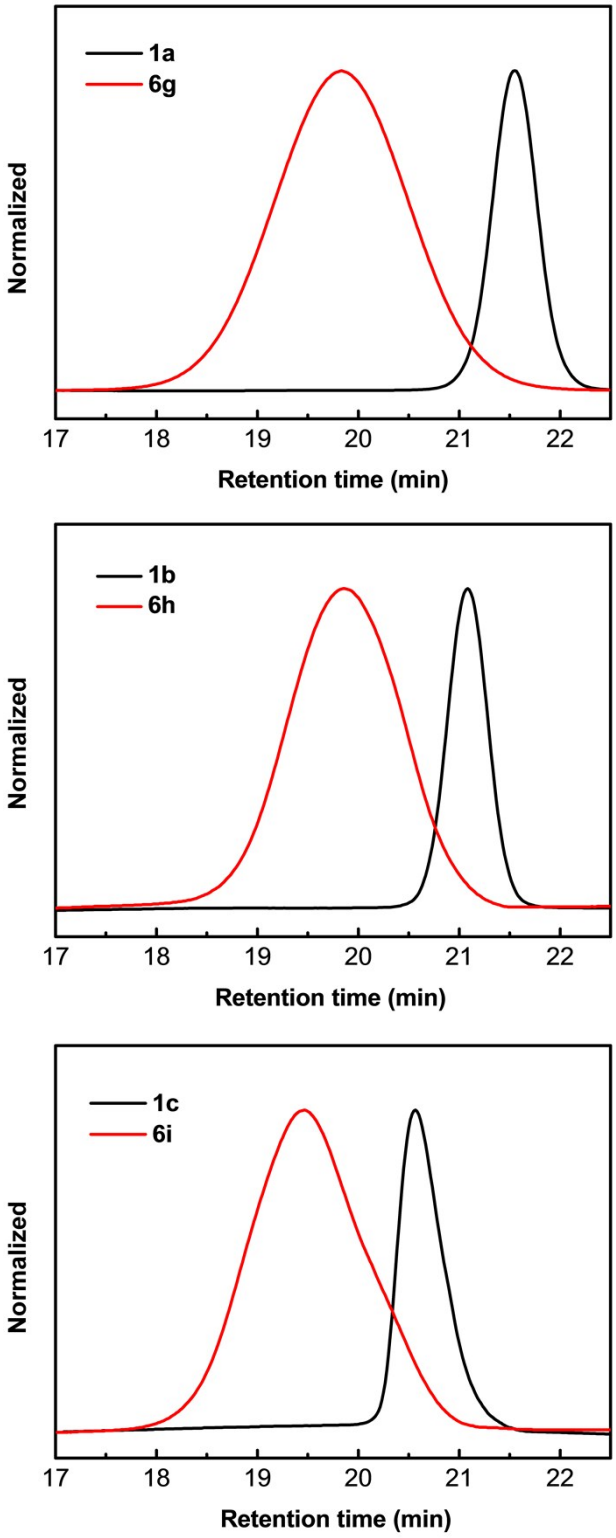

Fig. S10 GPC traces of **$MPEG_{1k}$-*epoxide*** (**1a-1c**) and **$(MPEG)_2(PCL)_2$** (**6g-6i**) prepared by the "One-pot" approach.

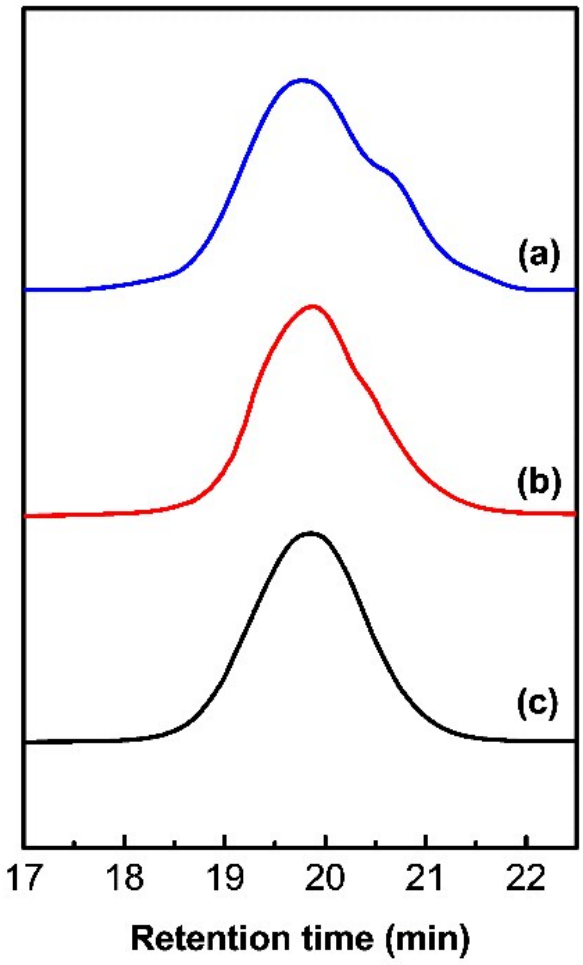

Fig. S11 GPC traces of the crude $(MPEG_{1k})_2(PCL_{2k})_2$ (6a) prepared by various mole ratio of *N*-phenylsydnone to $MPEG_{1k}$-*b*-PCL_{2k}(*MI*): (a) 1:1, (b) 2:1, (c) 4:1.

Table S1 Solubility of the *N*-phenylsydnone in various solvents[a]

Compond	Solvents[b]								
	DMF	**DMAc**	**DMSO**	**CH_2Cl_2**	**$CHCl_3$**	**CH_3OH**	**C_2H_5OH**	**EA**	**THF**
***N*-phenyl-sydnone**	++	++	++	++	++	++	++	++	++
	DEE	**DIOX**	**IPA**	**Tolene**	**Acetone**	**Hexane**	**PE**	**CYH**	**H_2O**
	++	++	++	++	++	+	+	+	-

[a] ++: soluble; +: partially soluble; -: insoluble

[b] Abbreviations: DMF, *N,N*-dimethylformamide; DMAc, *N,N*-dimethylacetamide; DMSO, dimethyl sulfoxide; EA, ethyl acetate; THF, tetrahydrofuran; DEE, diethyl ether; DIOX, 1,4-dioxane; IPA, isopropanol; PE, petroleum ether; CYH, cyclohexane.

Table S2 The Characterization of synthesized polymers

No.	Sample	Yield (%)	$M_{n,}$ [a] (KDa)	M_n [b] (KDa)	PDI[b]
3a	**MPEG$_{1k}$-(*OH*)(*FM*)**	80	1.3	2.1	1.01
3b	**MPEG$_{2k}$-(*OH*)(*FM*)**	87	2.3	2.7	1.01
3c	**MPEG$_{4k}$-(*OH*)(*FM*)**	85	4.3	4.1	1.05
4a	**MPEG$_{1k}$-*b*-PCL$_{2k}$(*MI*)**	95	3.6	3.1	1.19
4b	**MPEG$_{2k}$-*b*-PCL$_{1k}$(*MI*)**	96	3.6	3.3	1.17
4c	**MPEG$_{4k}$-*b*-PCL$_{4k}$(*MI*)**	98	8.1	7.7	1.23
5a	**(MPEG$_{1k}$)$_2$(*OH*)$_2$**	88	2.5	2.8	1.08
5b	**(MPEG$_{2k}$)$_2$(*OH*)$_2$**	90	4.5	4.0	1.06
5c	**(MPEG$_{4k}$)$_2$(*OH*)$_2$**	85	8.5	6.9	1.12
6a	**(MPEG$_{1k}$)$_2$(PCL$_{2k}$)$_2$**	92	7.3	6.3	1.20
6b	**(MPEG$_{2k}$)$_2$(PCL$_{1k}$)$_2$**	91	7.3	6.2	1.18
6c	**(MPEG$_{4k}$)$_2$(PCL$_{4k}$)$_2$**	86	16.3	14.4	1.24
6d	**(MPEG$_{1k}$)$_2$(PCL$_{2k}$)$_2$**	95	7.2	6.1	1.35
6e	**(MPEG$_{2k}$)$_2$(PCL$_{1k}$)$_2$**	93	8.3	7.3	1.23
6f	**(MPEG$_{4k}$)$_2$(PCL$_{4k}$)$_2$**	87	16.9	14.0	1.33
6g	**(MPEG$_{1k}$)$_2$(PCL$_{2k}$)$_2$**	88	7.3	6.6	1.22
6h	**(MPEG$_{2k}$)$_2$(PCL$_{1k}$)$_2$**	92	8.1	6.4	1.20
6i	**(MPEG$_{4k}$)$_2$(PCL$_{4k}$)$_2$**	86	17.7	14.6	1.23
6j	**(MPEG$_{2k}$)$_2$(PCL$_{2k}$)$_2$**	90	9.3	8.2	1.26
6k	**(MPEG$_{2k}$)$_2$(PCL$_{5k}$)$_2$**	85	15.1	12.1	1.31

[a] Determined by ^{1}H NMR;

[b] Determined by GPC in THF with calibrated PS standards at 35 °C.

Table S3 The efficiency of SMDC reaction under various mole ratio of reactants

No	Mole Ratio	Efficiency [a]
	***N*-phenylsydnone**: **$MPEG_{1k}$-*b*-PCL_{2k}(*MI*)**	**(%)**
1	1:1	~85
2	2:1	~94
3	4:1	~100

[a] Determined by ^{1}H NMR.