Supporting information

3-Miktoarm star terpolymers *via* Janus polymerization: One-step synthesis and self-assembly

*Yao Li[1], Moritz von der Lühe[2,3], Felix H. Schacher[2,3], Jun Ling[1,]**

[1] MOE Key Laboratory of Macromolecular Synthesis and Functionalization, Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, China.

[2] Institute of Organic Chemistry and Macromolecular Chemistry (IOMC), Friedrich-Schiller-University Jena, Lessingstraße 8, D-07743 Jena, Germany

[3] Jena Center for Soft Matter (JCSM), Friedrich-Schiller-University Jena, Philosophenweg 7, D-07743 Jena, Germany

Detailed mechanism of the Janus polymerization

The Janus polymerization involves three stages as shown in Figures S1 and S2. Since this manuscript, we prefer to use "three stages" instead of "three steps" as in *Macromolecules* 2014, 47, 2219-2225.

In Stage 1, the ring cleavage of epoxide generates both anionic (1A in Figure S1) and cationic (1B) ends. The anionic site initiates a homopolymerization of CL very slowly via anionic ring-opening polymerization (2A, 3A & 4A), while THF and CL co-propagate on the cationic site to produce a P(THF-*co*-CL) random segment (2B, 3B & 4B) with fast equilibriums between the end groups of 4B (or 4C) and 4B' (or 4C'). The kinetic plots in Figure S2 clearly show that the polymerization of anionic and cationic polymerization starts simultaneously in Stage 1.

The cationic site becomes dormant when the anionic site starts the rather fast propagation of CL, which leads the herein described Janus polymerization to enter Stage 2. In kinetic plots, the rate of CL polymerization is fast but THF is not consumed due to classic dormant species 5B in cationic ROP. As long as the CL conversion does not exceed 90%, the Janus polymerization is a living and controlled polymerization technique.

In Stage 3, when CL is mostly consumed, the cationic chain end is re-activated (6B) together with intermolecular coupling reactions between anionic and cationic ends, which produces multiblock copolymers. Only in this stage, chain-addition polymerization turns into a step-growth polymerization, leading to increased MW values and high polydispersity indices of products up to 2.

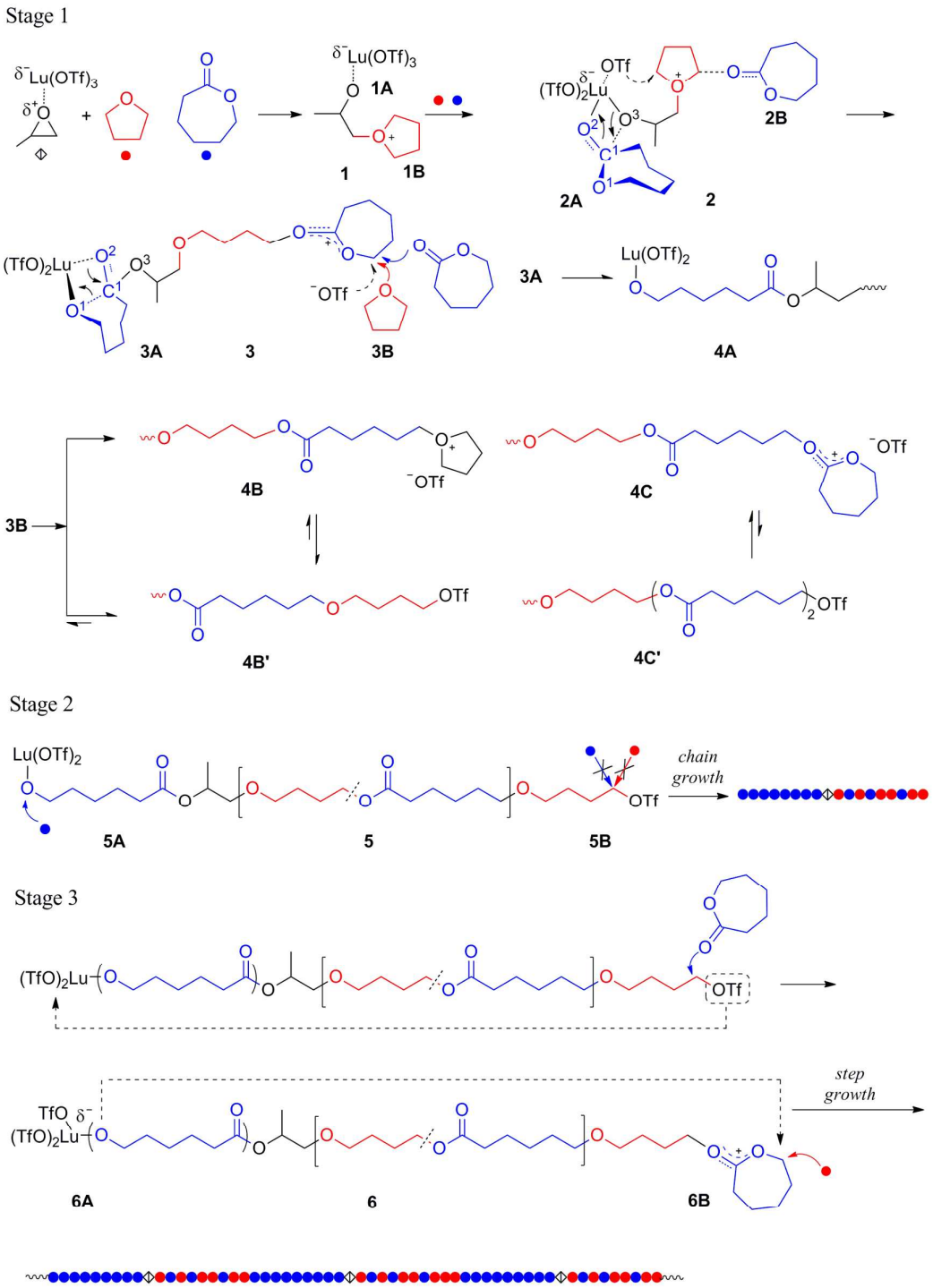

Figure S1. Detailed mechanism of the Janus polymerization of CL with THF. [Macromolecules 2014, 47, 2219-2225]

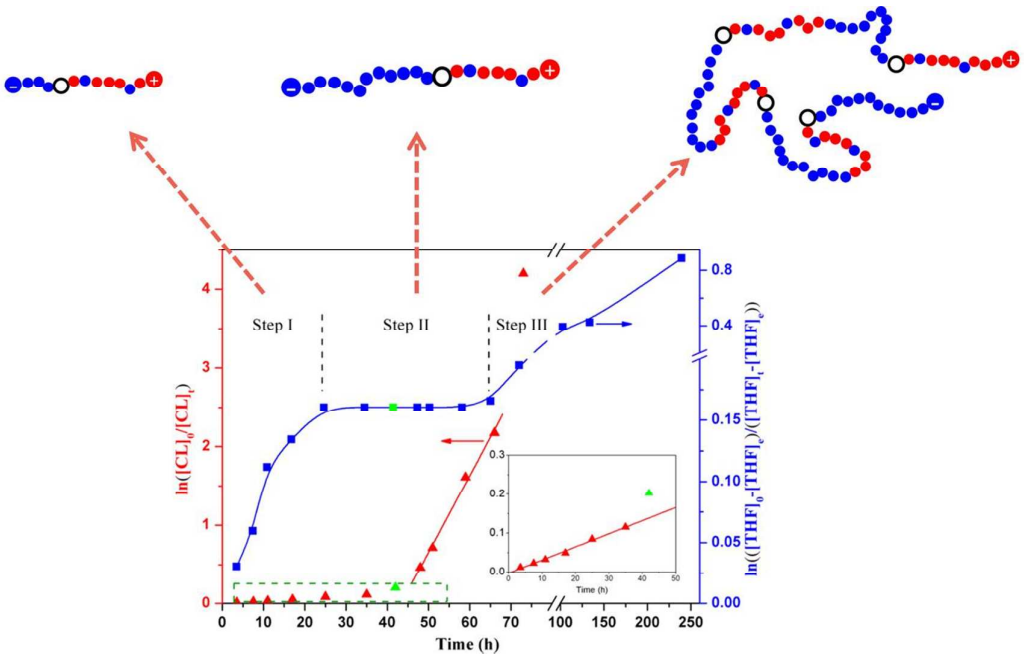

Figure S2. Kinetic plots of the Janus polymerization of CL with THF at 25 ºC catalyzed by $Lu(OTf)_3$ in the presence of PO and the schematic of polymers obtained during each steps. [Macromolecules 2014, 47, 2219-2225]

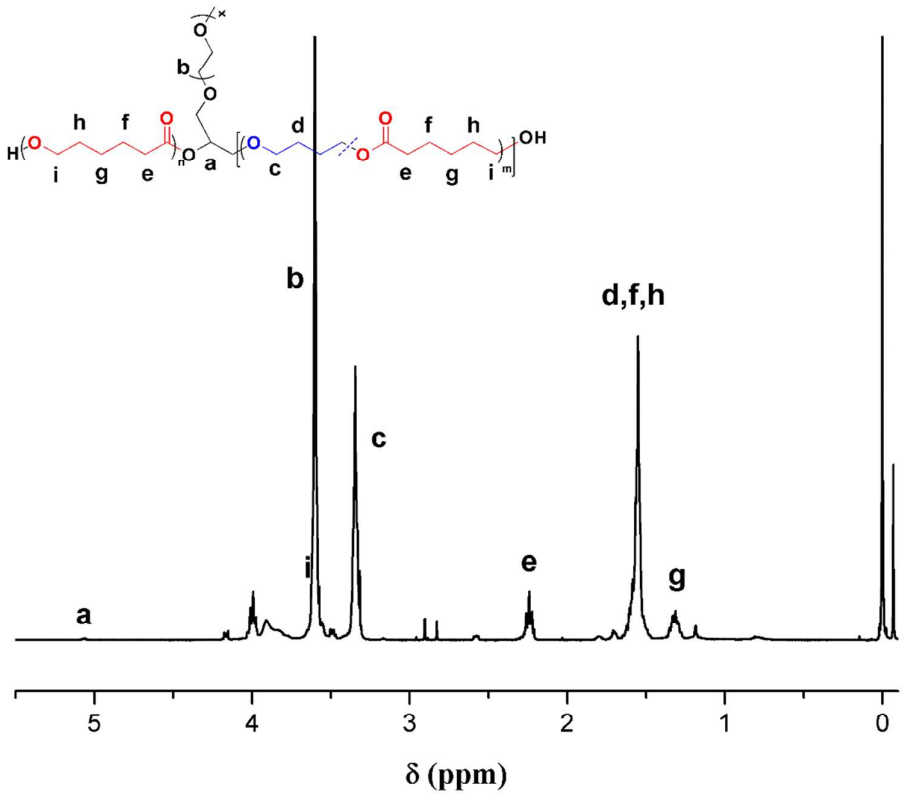

Figure S3. ^{1}H NMR spectrum of 3-miktoarm star terpolymer PEG_{45}-*star*-PCL_{8}-*star*-P(CL_{3}-*co*-THF_{25}) terminated by H_2O (Sample P2 in Table 1).

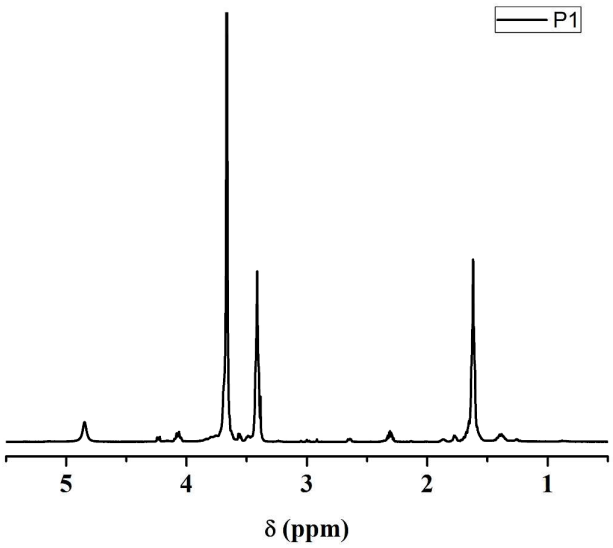

Figure S4. ^{1}H NMR spectrum of 3-miktoarm star terpolymer (Sample P1 in Table 1)

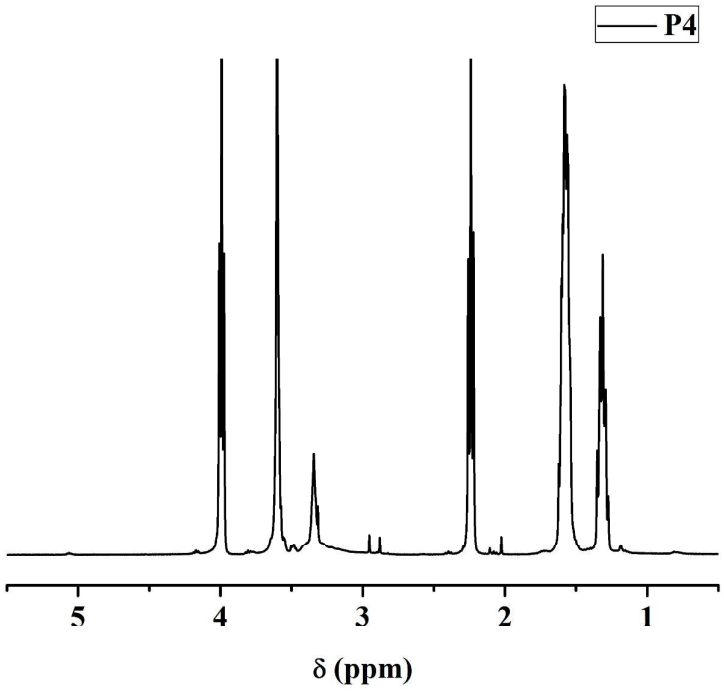

Figure S5. ^{1}H NMR spectrum of 3-miktoarm star terpolymer (Sample P4 in Table 1)

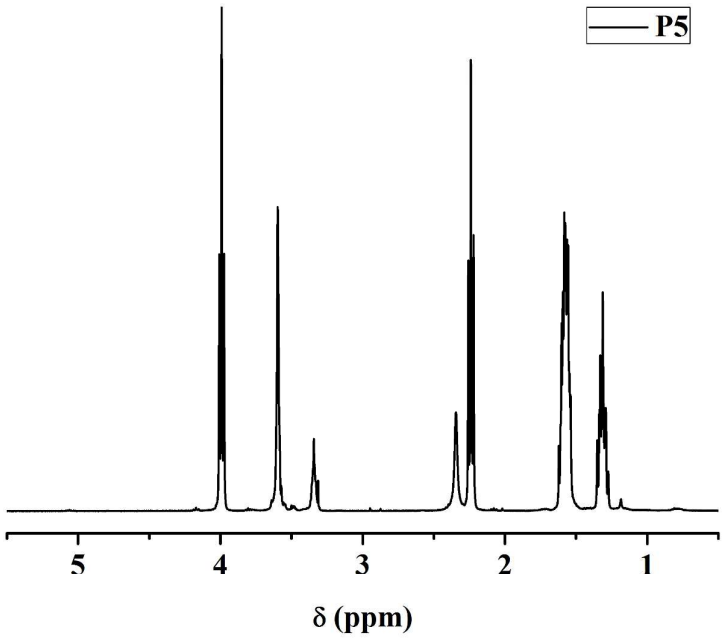

Figure S6. ^{1}H NMR spectrum of 3-miktoarm star terpolymer (Sample P5 in Table 1)

Table S1. Reactivity ratios measurement of THF and CL catalyzed by $Lu(OTf)_3$[a]

Run	Conversion of CL (%)[b]	Conversion of THF (%)[b]	$[CL]_0/[THF]_0$ (R)[c]	$d[M_{CL}]/d[M_{THF}]$ (ρ)[d]
1	6.01	2.40	9	11.11
2	5.42	1.40	4	3.92
3	3.45	2.01	2.333	2
4	3.08	1.67	1.5	1.38
5	2.3	3.22	1	0.72
6	2.23	4.16	0.667	0.38
7	4.27	7.32	0.25	0.15

[a] Copolymerizations were catalyzed by $Lu(OTf)_3$/PO with a molar ratio of 1:1 at 25 ºC. [b] Determined by taking a small amount of reaction mixture and dissolving in $CDCl_3$ for ^1H NMR analysis. Monomer conversions were calculated from the relative integration of the proton resonance of monomers and copolymers. [c] Feed molar ratio of CL to THF. [d] Calculated by ^1H NMR analysis with $CDCl_3$ as the solvent.

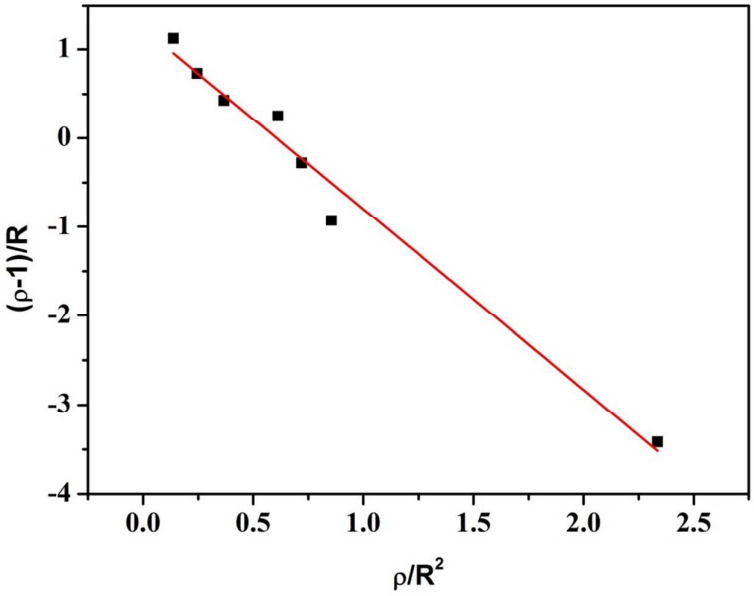

Figure S7. Plot of (ρ-1)/R *versus* ($ρ/R^2$) for the $Lu(OTf)_3$/PO catalyzed copolymerization of CL with THF and the linearly fitted lin whose intercept is r_1 [1.23, CL] and slope is $–r_2$ [2.03, THF] by the Fineman-Ross method.

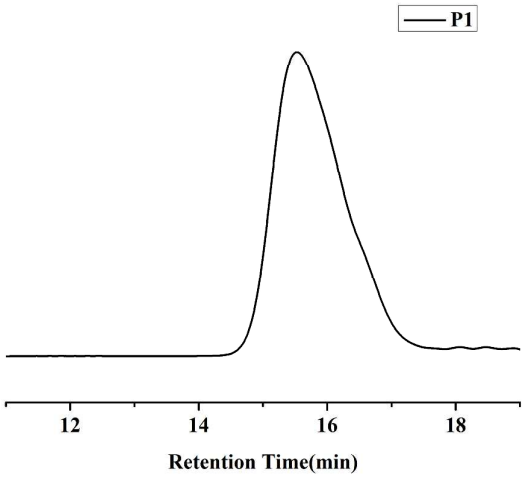

Figure S8. SEC trace of 3-miktoarm star terpolymer (Sample P1 in Table 1)

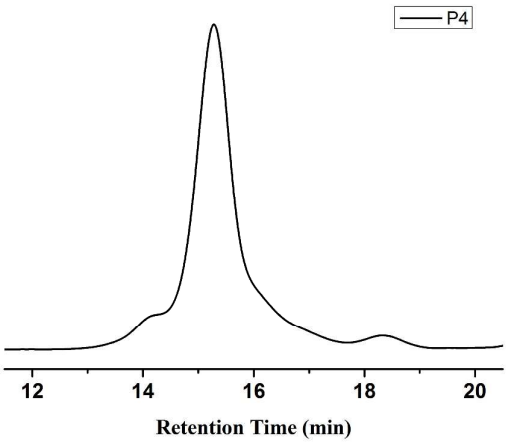

Figure S9. SEC trace of 3-miktoarm star terpolymer (Sample P4 in Table 1)

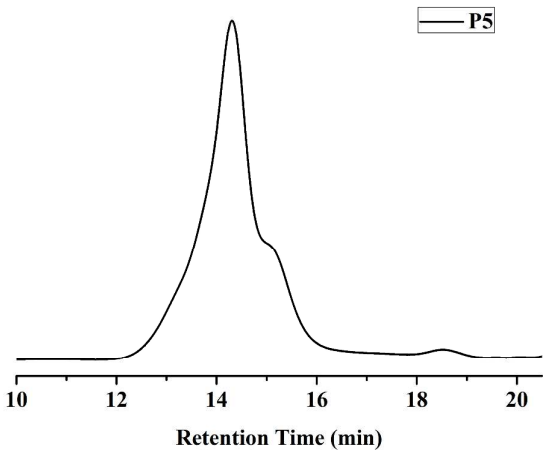

Figure S10. SEC trace of 3-miktoarm star terpolymer (Sample P5 in Table 1)

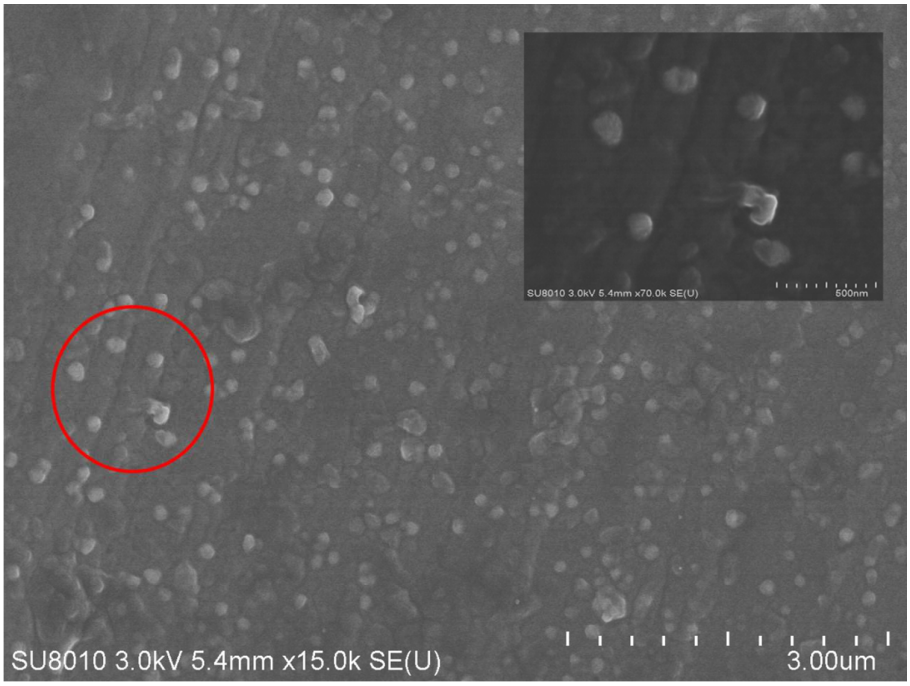

Figure S11. SEM images of vesicles self-assembled by 3-miktoarm star terpolymer PEG_{45}-*star*-PCL_{49}-*star*-P(CL_1-*co*-THF_{10}) (Sample P3 in Table 1) in water. Scale bar =3 μm.

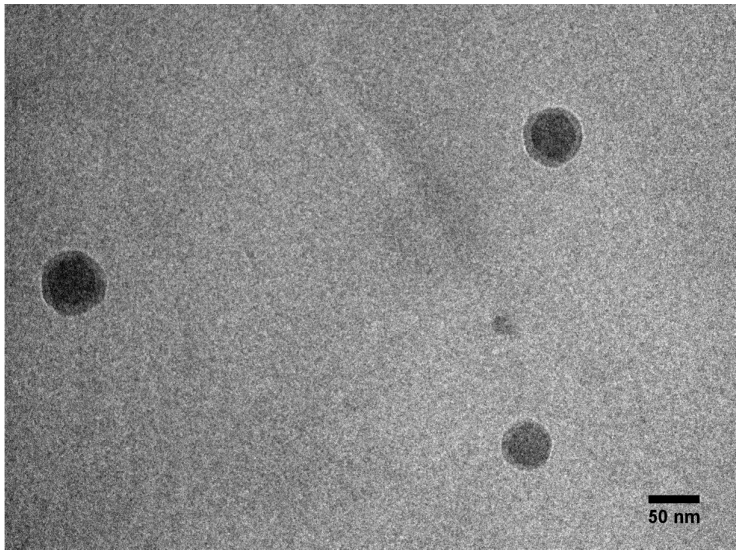

Figure 12. cryo-TEM image of vesicles self-assembled by 3-miktoarm star terpolymer PEG_{45}-*star*-PCL_{49}-*star*-P(CL_1-*co*-THF_{10}) (Sample P3 in Table 1) in water after thermal treatment. Scale bar = 50 nm.

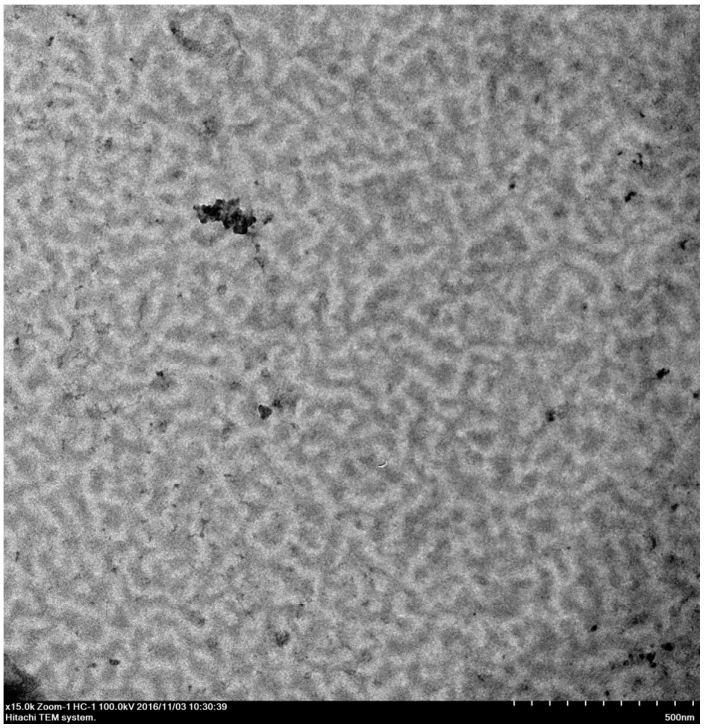

Figure S13. TEM image of phase separation by 3-miktoarm star terpolymer PEG_{45}-*star*-PCL_{49}-*star*-P(CL_1-*co*-THF_{10}) (Sample P3 in Table 1) in concentrated solution after annealing process. Scale bar = 500 nm.