Electronic Supplementary Information (ESI) for

Multifunctional Polymer Vesicles for Ultrasensitive Magnetic Resonance Imaging and Drug Delivery

Tianbin Ren, ^a Qiuming Liu, ^a Hang Lu, ^a Hongmei Liu, ^{b, c} Xin Zhang*^b and Jianzhong Du*^a

Fig. S1. ¹H NMR spectrum of PEO-Br macroinitiator.



Fig. S2. Correlation functions of DLS studies of un-cross-linked polymer vesicles prepared from PEO_{43} -b- $P(AA_{25}$ -stat- $tBA_{40})$ (Polymer 3) at various pH's. See Fig. 3 for the corresponding size distributions of polymer vesicles. The poor correlation function of un-cross-linked vesicles at pH 7.3 (Curve a) revealed that the PAA unit turned more hydrophilic because of the deprotonation of carboxylic groups upon NaOH addition, leading to the breaking of the vesicle membrane. However, for the membrane-cross-linked vesicles, even at pH 9 (see Fig. 7), the correlation function still fits well (not shown in this figure).



Fig. S3. Thermogravity analysis of superparamagnetic polymer vesicles based on (A) PEO₄₃*b*-P(AA₉-*stat*-*t*BA₅₆) (Polymer **2**) and (B) PEO₄₃-*b*-P(AA₂₅-*stat*-*t*BA₄₀) (Polymer **3**).



Fig. S4. Magnetic hysteresis loop of superparamagnetic vesicles prepared from PEO_{43} -*b*- $P(AA_{25}$ -*stat*-*t* $BA_{40})$ (Polymer 3).



Calculation procedures of ¹H NMR spectra in Fig. 1

The procedure of the determination of the compositions of block copolymers is listed below. According to the ¹H NMR spectra in Fig. 1, the degrees of polymerization of the four copolymers were calculated according to the following procedures.

Table S1. The areas of different peaks and the degrees of polymerization of different

| Spectrum | Polymer | a_{b} | a_d | a_{c+e} | Х | У |
|----------|---------|---------|-------|-----------|----|----|
| Α | 1 | 170 | 64.6 | 718.4 | 65 | |
| В | 2 | 170 | 65.4 | 639.8 | 9 | 56 |
| С | 3 | 170 | 64.8 | 487.7 | 25 | 40 |
| D | 4 | 170 | 64.7 | 265.8 | 50 | 15 |

copolymers

In **Table S1**, a_b , a_d , and a_{c+e} are the areas of the peaks b, d, and c+e in Fig.1. x and y are the degrees of PAA and P*t*BA. A, B, C and D represent the copolymer PEO₄₃-*b*-P*t*BA₆₅ (Polymer

I), PEO₄₃-*b*-P(AA₉-*stat*-*t*BA₅₆) (Polymer 2), PEO₄₃-*b*-P(AA₂₅-*stat*-*t*BA₄₀) (Polymer 3) and PEO₄₃-*b*-P(AA₅₀-*stat*-*t*BA₁₅) (Polymer 4).

We set that the integration area of peak b is 170, which corresponds to the amount of H in PEO_{43} (43 × 4 - 2 = 170). The area of peaks d and c+e in A, B, C and D are listed in Table

S1 according to the following equations:

A: according to peak d:
$$x = \frac{64.6}{170} \times \frac{43 \times 4 - 2}{1} = 64.6 \approx 65$$

according to peaks c+e: $x = \frac{718.4}{170} \times \frac{43 \times 4 - 2}{2 + 9} = 65.3 \approx 65$

B: according to peak d and peaks c+e

$$x + y = 65.4$$
$$2x + (2+9)y = 639.8$$
$$\rightarrow x = 9, y = 56$$

C: according to peak d and peaks c+e:

$$x + y = 64.8$$

2x + (2 + 9)y = 487.7
→ x = 25, y = 40

D: according to peak d and peaks c+e:

x + y = 64.72x + (2 + 9)y = 265.8 $\rightarrow x = 50, y = 15$