## SUPPORTING INFORMATION

# Strategy of "Block Blends" to Generate Polymeric Thermogels Versus That of One-component Block Copolymer

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#### S1 SUPPLEMENTARY METHODS

The dynamic Monte Carlo simulation was employed to investigate the thermogelling behavior of the block blends. The copolymer chain was coarse-grained to a model chain connected by beads. One bead corresponds to a few repeating units in the real copolymer chain, similar to a Kuhn segment.

Multiple self-avoiding chains were simulated in two-dimensional (2D) square lattices with periodic boundary condition applied in both directions (x, y) to eliminate the finite size effect (Figure S1A). A site was occupied by either a bead or a vacancy (solvent).



**Figure S1.** Schematic of models in simulations. (A) Coarse-grained models of block copolymers; (B) Micro-relaxation models used in simulations.

Larson bond fluctuation model,<sup>S1</sup> whose permitted bond length was 1 or  $\sqrt{2}$ , was utilized as the basic micro-relaxation mode, with a partial-reptation algorithm<sup>S2, S3</sup> as a supplement to promote the simulation efficiency.

The sampling method in simulations was Metropolis importance sampling,<sup>S4</sup> which endows the simulation process with a linear relation to the real physical process.<sup>S5</sup> In a dynamic Monte Carlo simulation, the time t is measured in units of Monte Carlo step (MCS). One MCS means the trial that every bead in the lattices has been randomly selected once on average.

The coarse-grained chain model was represented as  $A_xB_yA_x$ , where A and B represent hydrophobic and hydrophilic beads, respectively. The subscripts mean the numbers of beads in the corresponding blocks. For the relatively hydrophilic default block copolymer component P1 and hydrophobic default component P2, the values of *x* and *y* were x = 14, y = 36 and x = 28, y = 8, respectively. A coarse-grained solvent was treated as a vacancy and represented by V.

The concentration or volume fraction of model chains  $\varphi$  was calculated by

$$\varphi = \frac{N_{\text{bead}}}{L^2} \tag{S1}$$

Here  $N_{\text{bead}}$  represents the total number of beads in lattices;  $L^2$  is the number of square lattices. In the present simulations, L = 128.

For convenience, the default blends in simulations were distinguished by the fraction of the relatively hydrophilic copolymer P1 as

$$f_{\rm P1} = \frac{N_{\rm chain}({\rm P1}) \times N_{\rm seg}({\rm P1})}{N_{\rm chain}({\rm P1}) \times N_{\rm seg}({\rm P1}) + N_{\rm chain}({\rm P2}) \times N_{\rm seg}({\rm P2})}$$
(S2)

Here  $N_{\text{chain}}$  and  $N_{\text{seg}}$  represent the number of model chains and the number of beads per chain of different components indicated in the parenthesis, respectively; for a model chain  $A_x B_y A_x$ ,  $N_{\text{seg}} = 2x+y$ .

In our simulations, both nearest-neighbor and next-nearest-neighbor pairwise

interactions were considered. The energy parameter inputted directly was reduced energy  $\varepsilon_{ij}^*$ , where the subscripts *i* and *j* represent species in the system. The relationship between  $\varepsilon_{ij}^*$  and energy  $\varepsilon_{ij}$  is

$$\varepsilon_{ij}^* = \frac{\varepsilon_{ij}}{k_{\rm B}T} \tag{S3}$$

where  $k_{\rm B}$  is the Boltzmann constant, and *T* is the Kelvin temperature. An attractive interaction between *i* and *j* corresponded to  $\varepsilon_{ij}^* < 0$ , whereas a repulsive interaction meant  $\varepsilon_{ij}^* > 0$ .

The  $\varepsilon_{ij}^*$  between the same species was set to zero to simplify the simulation. The apparent interaction between the hydrophobic segment and water molecule is repulsive, thus the  $\varepsilon_{AV}^*$  in simulations was set positive. Based on some previous reports, <sup>S6, S7</sup> low molecular weight PEG and poly(lactic acid) (PLA, similar to PLGA) are miscible, thus the  $\varepsilon_{AB}^*$  was set negative by us. The values of the above energy parameters are listed in Figure 2A.

The hydrophilicity of the PEG block depends on temperature. Hence the relationship between the  $\varepsilon_{BV}^*$  and *T* can be utilized to model the systems at different temperatures. The determination of the quantitative relationship is described as follows.

The relationship between  $\varepsilon_{\rm BV}^*$  and the corresponding Huggins parameter  $\chi$  is

$$\varepsilon_{\rm BV}^* \sim \chi - 0.5 \tag{S4}$$

If the concentration effect is ignored, the  $\chi$  is related to temperature T as

$$\chi = a' + \frac{b'}{T} \tag{S5}$$

Here a' and b' are constants, corresponding to the contributions of the entropy and the

enthalpy, respectively.

Based on equation (S4) and equation (S5), the relation between  $\varepsilon_{BV}^*$  and T is

$$\varepsilon_{\rm BV}^* \sim a + \frac{b}{T} \tag{S6}$$

Here *a* and *b* are constants, dependent on the simulated system.

Upon heating, water is first a good solvent for the PEG block but gradually becomes its poor solvent. So, the  $\varepsilon_{BV}^*$  should evolve from negative to positive. On this base, a judgement for *a* and *b* is a > 0 and b < 0. After lots of trial-and-error computer experiments, the quantitative relationship between the  $\varepsilon_{BV}^*$  and *T* in this work was

$$\varepsilon_{\rm BV}^* = 2.1 - \frac{671}{T}$$
 (S7)

Taking the default model chains as example, the general simulation process is described as follows: initially, corresponding to the preset  $\varphi$  and  $f_{P1}$ , P1 and P2 model chains were put into the 2D lattice system with lattice number of  $L^2 = 128 \times 128$ . After sufficiently randomized at the athermal state with all reduced energies set to zero, the multiple self-avoiding chains were relaxed at a predetermined temperature based on equation (S7). At each temperature, after relaxed for  $5 \times 10^6$  MCS to reach equilibrium, the statistics for thermodynamic parameters was carried out during the following  $5 \times 10^6$  MCS. The sampling interval was  $10^3$  MCS, thus total 5000 time points were sampled for time average in a run.

Ten independent runs were generally conducted for ensemble average.

The Fortran codes for simulations were written by the authors, and run on a computer with a 3.0 GHz CPU.

#### **S2** SUPPLEMENTARY RESULTS

*S2.1* **Definitions of aggregates in simulations.** For the convenience of statistics, some terms of the aggregates were defined in our simulations. These terms are described in detail in the main manuscript. Figure S2 is the schematic illustration of two essential aggregate terms, aggregate-total and aggregate-core.



**Figure S2.** Schematic illustrations of aggregate-total and aggregate-core of the ABA block copolymers in a selective solvent.

The average size of the aggregates in a system was characterized by the weight average molecular weight of aggregates as

$$M_{\rm w}(\text{aggregate}) = \frac{\Sigma M_i^2}{\Sigma M_i}$$
(S8)

where  $M_i$  represents the number of beads in the *i*-th aggregate. For aggregate-total and aggregate-core, this parameter could be called  $M_w$ (aggregate-total) and  $M_w$ (aggregate-core), respectively.

In order to eliminate the interference of the bridge between micelles to some statistics, we took the semi model chain equivalent to half of the ABA model chain into our statistics, where one  $A_x B_y A_x$  model chain was treated as two  $A_x B_{y/2}$  semi

model chains.

*S2.2* Aggregate distributions of different systems at 5°C. In a block blend, co-assemblies of the copolymers at low temperatures are precursors of the further aggregation into a micelle network. To have a gloss understanding of the co-assemblies, aggregate distributions of different systems at 5°C were calculated. The aggregate distribution was characterized from two aspects, size distribution and radius-of-gyration ( $R_g$ ) distribution. The aggregate size here was defined as the number of semi model chains in an aggregate, and the  $R_g$  of an aggregate was calculated by

$$R_{\rm g} = (R_{\rm g}^{2})^{0.5} = \left(\frac{\Sigma m_{i} r_{i}^{2}}{\Sigma m_{i}}\right)^{0.5}$$
(S9)

where  $m_i$  represents the mass of the *i*-th bead in an aggregate, and is equal to 1 for all beads;  $r_i$  is the position vector from the *i*-th bead to the centroid of the aggregate.

The aggregate size mainly corresponded to the aggregate mass, and the  $R_g$  of the aggregate mainly corresponded to the aggregate volume.

From Figure S3A, the size distribution of aggregate-core in the P1 system was very narrow and mainly focused on small values, while that in the system of the relatively hydrophobic block copolymer P2 was wide. The aggregate-core size distribution of the block blend system with P1:P2 = 0.5:0.5 ( $f_{P1} = 0.50$ ) fell in between. The similar phenomenon was observed in the  $R_g$  distribution of the aggregate-core.



**Figure S3.** Simulated distribution of aggregates in the indicated different systems at 5°C. (A) Mass distribution of size (top) and  $R_g$  (bottom) of aggregate-core; (B) Mass distribution of size (top) and  $R_g$  (bottom) of aggregate-total. The aggregate size was represented by the number of semi model chains in the aggregate. The volume fraction  $\varphi$  was 0.25.

Figure S3B depicts the aggregate-total distributions of different systems. Besides a high fraction of small aggregates, a fraction peak corresponding to large aggregates was observed. With a decrease of  $f_{P1}$ , the fraction of the small aggregates decreased and the fraction of the large aggregates increased; besides, the large aggregate peak moved to a higher size position.

The  $R_{\rm g}$  evolution tendencies of the small and large aggregate-totals were consistent

with their size evolution tendencies. But the peak corresponding to the  $R_g$  of large aggregates moved to a lower position as the  $f_{P1}$  decreased, which implied that the large aggregate-total in a lower  $f_{P1}$  system was more compact.

The relatively smooth distribution curves of all these parameters in the block blend aqueous system illustrated the co-assembly of the two amphiphilic copolymers.

*S2.3* Self-aggregate of one component in block blends at 5°C. In our simulations, we treated both self-aggregate of P1 and self-aggregate of P2 to analyze the extent of the system homogeneity. The self-aggregate was characterized by the aggregate-core of one component (P1 or P2). This term was similar to the aggregate-core, but only one component was displayed and joined in some statistics, as schematically shown in Figure S4A.

The average size of the aggregate-core of one component was quantified as

$$M_{\rm w}(\text{aggregate} - \text{core}) \text{ of one component} = \frac{\Sigma M_i^2}{\Sigma M_i}$$
 (S10)

where  $M_i$  represents the number of beads in the *i*-th aggregate-core of one component.

 $M_{\rm w}$ (aggregate-core) of P1 and  $M_{\rm w}$ (aggregate-core) of P2 at 5°C as a function of  $f_{\rm P1}$  are shown in Figures S4B and S4C, respectively. The  $M_{\rm w}$ (aggregate-core) of P1 was always low according to our dynamic Monte Carlo simulations of multiple self-avoiding chains, indicating that the relatively hydrophilic block copolymer P1 was well dispersed at all  $f_{\rm P1}$ .



**Figure S4.** Simulated self-aggregate of one component in different block blends at 5°C. (A) Schematic of the aggregate-core of P1 and aggregate-core of P2; (B-C)  $M_w$ (aggregate-core) of P1 and  $M_w$ (aggregate-core) of P2 of systems with indicated  $\varphi$  as a function of  $f_{P1}$ . Two figures in (B) show the same result of  $M_w$ (aggregate-core) of P1 against  $f_{P1}$  with different ordinate ranges. The vertical line in (C) indicates the turning point of the  $M_w$ (aggregate-core) of P2 against  $f_{P1}$ .

With a decrease of  $f_{P1}$ , the evolution of  $M_w$ (aggregate-core) of P2 exhibited a fast increase following a slight increase (Figure S4C). The turning points for all systems with different  $\varphi$  were similar and around  $f_{P1} = 0.33$ . The fast increase implied that the P2 preferred to self-aggregate rather than co-assemble with P1 in systems with low  $f_{P1}$ . The co-assembly mainly existed in the slight increase region with high  $f_{P1}$ . Thus the mixing tendency in systems with low  $f_{P1}$  became poor, and the system in this case might correspond to a poorly soluble or even insoluble system in experiments. *S2.4* Morphology evolution of thermogellable block blends upon heating. The schematic of general morphology evolution of thermogellable block blends upon heating is shown in Figure S5. For a thermogellable block blend, many crew-cut micelles disperse in the system at low temperatures. The bridge structure forms spontaneously between different micelles. With an increase of temperature, the reversed thermosensitive B block results in the collapse of the micellar corona, unfavorable for the formation of the bridge linking two distant cores. Therefore, the number of bridges  $N_{\text{bridge}}$  decreases.



**Figure S5.** Schematic aggregation process of thermogellable block blends upon heating.  $N_{\text{bridge}}$  and  $N_{\text{channel}}$  represent the number of hydrophilic bridges and the number of hydrophobic channels, respectively. For gel-1, both the hydrophilic bridge and the hydrophobic channel act as the cross-linking points; for gel-2, the main cross-linking point of the network is hydrophobic channel.

At higher temperatures, when the collapsed corona cannot totally wrap the micellar core, the semi-bald micelles form. Owing to the instability of the hydrophobic exposed core area of the semi-bald micelles, micelles aggregate and a hydrophobic channel forms at the core-to-core location. The previous bridge between cores disappears.

With the help of the bridge already existing in abundance, a small number of

hydrophobic channels may lead to a whole network. This state is named gel-1 with the hydrophilic bridge as the main cross-linking point. As the temperature increases further, the more collapse of the corona leads to more semi-bald micelles. The number of hydrophobic channels increases dramatically and the hydrophobic channel becomes the dominant cross-linking point in this new state (gel-2). In the whole process upon heating, the number of bridges always decreases.

*S2.5* Evolution of aggregate distribution upon heating. The aggregate distribution was characterized by the size distribution and the  $R_g$  distribution. The typical system selected in this part was a block blend with  $f_{P1} = 0.50$  and  $\varphi = 0.25$ . From Figure S6A, with an increase of temperature, an evident fraction peak corresponding to large aggregate-cores appeared and gradually moved to larger values, indicating the occurrence of aggregation. The size distribution evolution of the aggregate-total was similar to that of the aggregate-core.



**Figure S6.** Evolution of aggregate size distribution upon heating in our simulations. (A) Mass distribution of the size of aggregate-core; (B) Mass distribution of the size of aggregate-total. The aggregate size was represented by the number of semi model chains in an aggregate. The model chains here were the default ones. The  $f_{P1}$  of the system was 0.50 and the  $\varphi$  was 0.25.

The aggregation could be similarly observed from the  $R_g$  distribution as shown in Figure S7. As the temperature increased, the area of the peak of small aggregate-cores decreased while that of large aggregate-cores increased; besides, the peaks of large aggregate-cores gradually moved to larger size values. The decrease of the small aggregate fraction and the increase of the large aggregate fraction upon heating were also observed in the  $R_g$  distribution of aggregate-total. But the peaks of big aggregate-totals moved to lower values upon heating, which was ascribed to the volume shrinkage of the aggregates.



**Figure S7.** Evolution of  $R_g$  distribution upon heating. (A) Mass distribution of  $R_g$  of aggregate-core; (B) Mass distribution of  $R_g$  of aggregate-total. The model chains here were the default ones. The  $f_{P1}$  of the system was 0.50 and the  $\varphi$  was 0.25.

S2.6 Simulated thickness of aggregate's corona. Thickness of the corona  $d_{corona}$  of aggregate defined in simulations is schematically described in Figure S8. The calculation formula of  $d_{corona}$  was

$$d_{\text{corona}} = \langle R_{\text{g}}(\text{aggregate} - \text{core}) - R_{\text{g}}(\text{block A in core}) \rangle_{m} \qquad (S11)$$

where the  $R_g$ (aggregate-core) and  $R_g$ (block A in core) represent the radius of gyration  $R_g$  of an aggregate-core and  $R_g$  of total A blocks in this aggregate-core, respectively;  $<>_m$  means average by the aggregate-core mass.



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gyration radius of an aggregate  $R_g = (R_g^2)^{0.5} = (\sum m_i r_i^2 / \sum m_i)^{0.5}$  i = 1, 2, 3, ..., N  $m_i^2$  the mass of *i*-th bead in an aggregate  $r_i^2$  vector from *i*-th bead to the aggregate centroid N: number of beads in an aggregate

 $d_{corona} = \langle R_{a}(aggregate-core) - R_{a}(block A in core) \rangle_{m}$ 

<> ": averaged by mass of aggregate-cores



**Figure S8.** Schematic of corona thickness and its evolution. (A) Definition of  $d_{corona}$  in simulations; (B) Schematic illustration of different cases of the different relationships between  $R_g$ (aggregate-core) and  $R_g$ (block A in core) in typical systems.

At low temperatures with  $\varepsilon_{AV}^* > \varepsilon_{BV}^*$ , the hydrophilic B block mainly distributed outside an aggregate-core. Based on the  $R_g$  formula (equation S9), the  $R_g$ (aggregate-core) was bigger than  $R_g$ (block A in core), thus  $d_{corona} > 0$  in this case.

Then as temperature increased, the  $d_{corona}$  decreased due to the collapse of micellar corona caused by the increasingly less hydrophilicity of the B block upon heating. Extreme cases occurred at extremely high temperatures when  $\varepsilon_{AV}^* < \varepsilon_{BV}^*$ , the B block preferred to distribute inside an aggregate-core. For systems with high  $f_{P1}$ , the volume fraction of B block was high, thus the B blocks couldn't be sufficiently wrapped by the A blocks and were still mainly located outside the aggregate-core. The  $R_g(aggregate-core)$  was still bigger than the  $R_g(block A \text{ in core})$  and  $d_{corona} > 0$ . In systems with medium  $f_{P1}$ , the B blocks with medium volume fraction were focused on the inside of an aggregate-core. As a result, the block A in the core has many "hollows" caused by the B block, which decreased the contributions of the small r in the  $R_g(block A \text{ in core})$  and made the  $R_g(block A \text{ in core})$  bigger than the  $R_g(aggregate-core)$ . Therefore,  $d_{corona} < 0$  in this case. In systems with low  $f_{P1}$ , the few B blocks would be evenly dispersed inside the aggregate-cores. The  $d_{corona}$  was near zero due to the almost negligible influence of the few dispersed B blocks on  $R_g(aggregate-core)$  and  $R_g(block A \text{ in core})$ .

*S2.7* Fractions of aggregate-core types at different temperatures. The fractions of aggregate-cores composed of only P1, only P2 and mixture of P1 and P2 at different temperatures were calculated. The states at 5°C, 37°C, 40°C and 60°C in Figure S9 corresponded to the sol, gel-1, gel-2, and precipitate states, respectively. From Figures S9A and S9B, if only n > 1 was considered, where n means the number of the semi model chains in an aggregate-core, the major aggregate-core in system was the mixed one at all temperatures. This phenomenon was more evident in the simulated results of mass fraction.



**Figure S9.** Statistics of fractions of different aggregate-cores. Number fractions (A) and mass fractions (B) of aggregates of only P1, only P2 and the mixture of P1 and P2 at indicated temperatures. The  $f_{P1}$  of the system was 0.50 and the  $\varphi$  was 0.25.

After the case n = 1 was considered, the aggregate-core of only P1 became the majority in number, but the mixed one was still dominant in mass. With an increase of temperature, both for n > 1 and  $n \ge 1$ , the increase of the mass fraction of the mixture aggregate-core implied the fusion of the aggregate-core with only one component with other aggregate-cores.

S2.8 Evolution of the number of hydrophobic pairwise contacts  $(N_{pair})$  upon heating. If a contact (nearest neighbor or next-nearest neighbor) occurred between

two beads, these two beads were called a pairwise contact. There were two types of hydrophobic beads, P1-A and P2-A in the simulation system, thus the hydrophobic pairwise contacts contained three types,  $A_{P1}A_{P1}$ ,  $A_{P1}A_{P2}$ , and  $A_{P2}A_{P2}$ .

Although the evolution of one contact might be influenced by others with complex reasons, the results from Figure S10 released some valuable information. At low temperatures before thermogelation, a slight increase of  $N_{pair}$  of  $A_{P2}A_{P2}$  indicated a self-aggregate of the A blocks of P2 component (the relatively hydrophobic block copolymer), providing assistant evidence that the P2 copolymer was the main component of the hydrophobic channel. Another noticeable point was that the  $N_{pair}$  of  $A_{P1}A_{P2}$  increased from around 20°C, which might result from the fusion of the small aggregates mainly composed of P1 with the large aggregates mainly composed of P2.



**Figure S10.** Hydrophobic pairwise contacts evolution with an increase of temperature. The  $f_{P1}$  of the system was 0.50 and the  $\varphi$  was 0.25.

*S2.9* Roles of P1 and P2 in the percolated micelle network. Figure S11 presents a snapshot of the percolated micelle network in a block blend with P1:P2 = 0.5:0.5 ( $f_{P1}$ 

= 0.50). In order to distinguish the roles of P1 component and P2 component in the network, we also show the snapshots of block blends with only P1-A or only P2-A extracted.



Blends of Amphiphilic Block Copolymers with P1:P2 = 0.5:0.5

**Figure S11.** Whole snapshot, the snapshot of P1-A and the snapshot of P2-A of the percolated micelle network. The  $f_{P1} = 0.50$  (P1:P2 = 0.5:0.5) and  $\varphi = 0.25$ . The temperature was 37°C. The black arrow in the snapshot of P2-A indicates the possible position of the hydrophobic channel.

From Figure S11, P1-A mainly assembled into small aggregates from the snapshot of only P1-A. Different from the snapshot of only P1-A, many long irregular aggregates were observed in the snapshot of only P2-A, indicating the skeleton role of the relatively hydrophobic P2 component in the network. Some narrow areas of the P2-A aggregate might correspond to the hydrophobic channel. Combined with the whole snapshot, the relatively hydrophilic P1 component mainly dispersed outside the network skeleton of the relatively hydrophobic P2 component.

#### S2.10 Two aspects to illustrate the main component of the hydrophobic channel.

The hydrophobic channel was mainly composed of P2 copolymer. Such a viewpoint could be further interpreted from two aspects, as schematically illustrated in Figure S12.



Figure S12. Schematic illustrations of the favorite of P2 as the main component in the

hydrophobic channel between semi-bald micelles.

First, the short length of the B block (hydrophilic block) of the P2 copolymer (relatively more hydrophobic block copolymer) endows the core area under the corona area with more possibility to expose when the corona collapses. Thus this core area is more likely to be a bald area in a semi-bald micelle, further leading to the well formation of the hydrophobic channel between semi-bald micelles.

Second, the main component of the hydrophobic channel can be analyzed from an aspect of chain conformation entropy. The entropy *S* of a system is

$$S = k \ln \Omega \tag{S12}$$

where *k* is the Boltzmann constant and  $\Omega$  is the number of the microstates. Thus the entropy change  $\Delta S$  in a process is

$$\Delta S = S_{\text{new}} - S_{\text{old}} = k \ln \Omega_{\text{new}} - k \ln \Omega_{\text{old}} = k \ln \left(\frac{\Omega_{\text{new}}}{\Omega_{\text{old}}}\right)$$
(S13)

where the subscripts indicate the states before and after the evolution process. The entropy loss means  $\Delta S < 0$ . More entropy loss means less tendency of a process in light of thermodynamic driving force.

A hydrophobic channel with significant steric hindrance must decrease the number of the available conformations of the hydrophilic B block, which is the origin of an entropy loss. For a longer B block in the relatively more hydrophilic block copolymer P1, this entropy loss is of more significance, thus a shorter B block in the relatively more hydrophobic block copolymer P2 favors being located in the channel position. Hence, it is reasonable that the hydrophobic channel in the block blend might mainly be composed of the relatively hydrophobic block copolymer.

*S2.11* Heterogeneous spatial distribution of different components in micelle units of the gel network. Solvent coordination numbers of the indicated bead types were calculated, as results shown in Figure S13. A higher coordination number of a type of bead indicates that this type of bead is closer to the outside of the aggregate. From the statistics, the hydrophilic P1 preferred to be located outside the aggregate while the hydrophobic P2 preferred to be located inside the aggregate. This spatial heterogeneity maintained until the precipitate formation.



**Figure S13.** Evolution of the heterogeneous distribution of P1 and P2 in aggregates with temperature. Solvent coordination numbers of the indicated bead types were calculated.  $A_{P1}V$ ,  $A_{P2}V$ ,  $B_{P1}V$  and  $B_{P2}V$  represent the solvent (V) coordination numbers of the A and B beads of the subscripted indicated chains, respectively. In this typical system,  $f_{P1} = 0.5$  and  $\varphi = 0.25$ .

### SUPPLEMENTARY REFERENCES

(S1) Larson, R. G.; Scriven, L. E.; Davis, H. T. Monte-Carlo simulation of model amphiphilic oil-water systems. *J. Chem. Phys.* **1985**, *83*, 2411-2420.

(S2) Hu, W. B. Structural transformation in the collapse transition of the single flexible homopolymer model. *J. Chem. Phys.* **1998**, *109*, 3686-3690.

(S3) Ji, S. C.; Ding, J. D. Spontaneous formation of vesicles from mixed amphiphiles with dispersed molecular weight: Monte Carlo simulation. *Langmuir* **2006**, *22*, 553-559.

(S4) Metropolis, N.; Rosenbluth, A. W.; Rosenbluth, M. N.; Teller, A. H.; Teller, E. Equation of state calculations by fast computing machines. *J. Chem. Phys.* **1953**, *21*, 1087-1092.

(S5) Binder, K.; Heermann, D. W. *Monte Carlo simulation in statistical physics*, Springer: Berlin, 2010.

(S6) Li, T. Q.; Zhang, J. Y.; Schneiderman, D. K.; Francis, L. F.; Bates, F. S. Toughening glassy poly(lactide) with block copolymer micelles. *ACS Macro Lett.* **2016**, *5*, 359-364.

(S7) Takhulee, A.; Takahashi, Y.; Vao-soongnern, V. Molecular simulation and experimental studies of the miscibility of polylactic acid/polyethylene glycol blends. *J. Polym. Res.* **2016**, *24*, 8.