Supporting Information

PhotoATRP-Based Fluorinated Thermosensitive Block Copolymer for Controllable Water/Oil Separation

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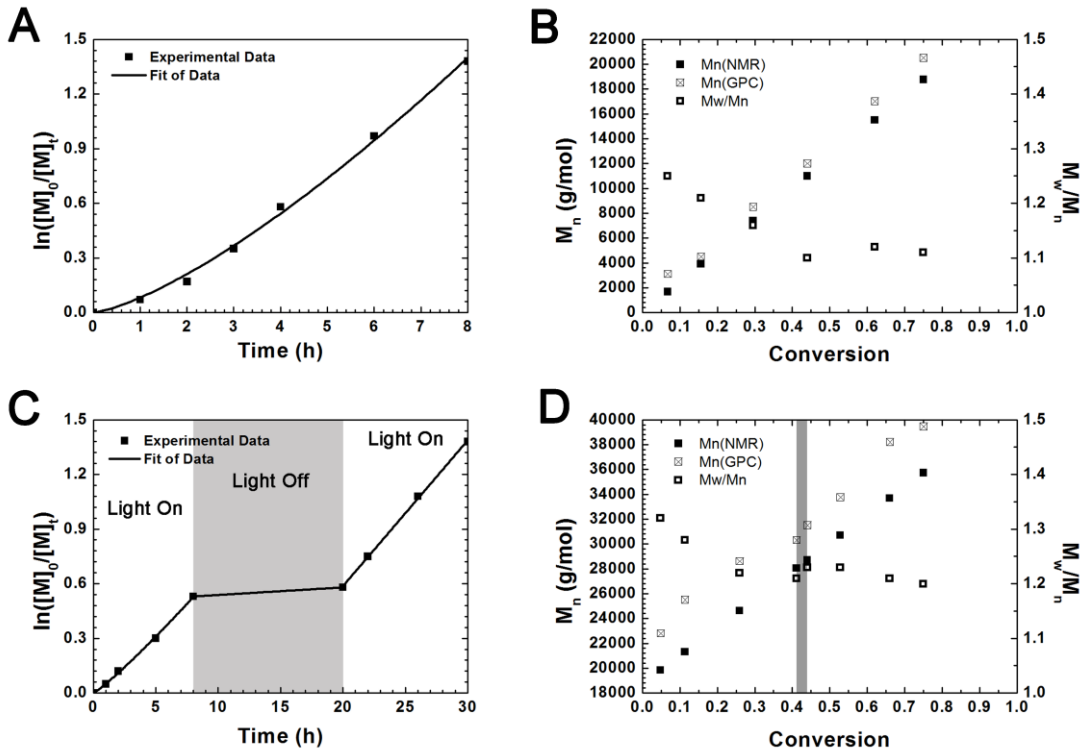

Figure S1. Kinetic outcomes of the photoATRPs: (A) the semilogarithmic kinetic plot and (B) the evolution of M_n and M_w/M_n with conversion for the photoATRP of HFBMA; (C) the semilogarithmic kinetic plot and (D) the evolution of M_n and M_w/M_n with conversion for photoATRP of NIPAAm

Kinetics Study. Figure S1 shows the kinetic plots for both polymerization processes induced by UV irradiation. Both reactions follow pseudo-first-order kinetics after a short induction period as depicted in Figure S1A and S1C, which indicate a constant concentration of radicals in systems at steady-state. The linear evolution of M_n and the level-off of M_w/M_n with the conversion in Figure S1B and S1D for both polymerizations imply a typical feature of living polymerization. The relatively broader M_w/M_n at steady-state (≈1.20) of $PHFBMA_{75}$-*b*-$PNIPAAm_{150}$ than that (≈1.10) of $PHFBMA_{75}$-Cl is attributed to the slightly inefficient initiation of macroinitiator. These kinetic characteristics coincide with those obtained in our previous simulation work.[1] The induction period is likely caused by the slow reduction of CuII to CuI

under UV irradiation and the slow initiation activity of EibBr initiator. The deviation of molar mass by GPC from that by ^{1}H NMR may be due to the different hydrodynamic volume between the resulting polymers and narrow PMMA standards.

Another advantage of photoATRP is its temporal controllability. In the chain extension reaction, the "on/off" temporal control during polymerization was investigated by using successive light on and off condition. As shown in Figure S1C and S1D, the reaction is performed under UV irradiation for 8 h, the monomer conversion is approximately 41% and the value of M_w/M_n decreases from 1.32 to 1.21. At the moment, the UV light is turned off and the polymerization mixture is kept in the reaction box for 12 h. One can find that the polymerization is almost stopped, the monomer conversion increases only 3% during this period. This is because the activator CuI is no longer generated by the photo-reduction of CuII in the dark, and only the residual activator can maintain the polymerization. When the mixture is re-irradiated by UV light, the polymerization is re-started. Figure S1C demonstrates that the reaction rate keeps the same as that of the first reaction period, which indicates that the nature of polymerization is not affected by the interruption of light source. After additional 10 h, the monomer conversion reaches 75% (Figure S1D), and the evolution of M_w/M_n undergoes a slight increase and followed by a decrease. These results highlight that the photoATRP used here is a new and facile synthetic technique for the synthesis of functional polymers with environment friendly (low catalyst dosage and without heating), well structural controllability (low PDI), and temporal controllability (stop and restart by on/off light switch) features, which is

valuable for the further investigation of its mechanism and future applications.

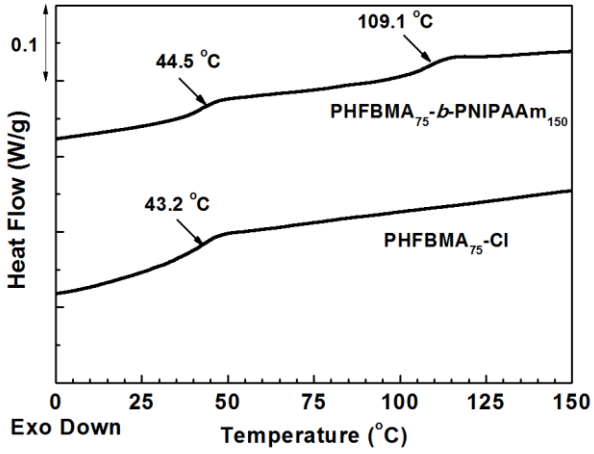

Figure S2. DSC heating curves of $PHFBMA_{75}$-Cl and $PHFBMA_{75}$-*b*-$PNIPAAm_{150}$

Thermal Property of Fluorinated Polymers. Compared to random copolymer, block copolymer has an abrupt change in composition at the block joint point, which covalently bonds the chemically incompatible blocks and maintains their unique properties. The glass transition behaviors of resulting polymers were investigated by DSC as shown in Figure S2. The fluorinated homopolymer possesses a single glass transition temperature (T_g) at 43.2 °C. In contrast, the block copolymer exhibits two T_gs, which locate at 44.5 °C associated with the PHFBMA block and 109.1 °C assigned to the PNIPAAm block. In general, the T_g of PNIPAAm homopolymer ranges from 110 to 150 °C depending on the stereoregularity and molar mass.[2] The relative higher T_g of PHFBMA block and lower T_g of PNIPAAm block than that of their homopolymer are likely caused by the synergistic effect between these two blocks, namely the internal plasticization effect, which is introduced by incorporating a flexible segment (PHFBMA).[3,4] In addition, the external plasticization effect of water on PNIPAAm facilitating disentanglement of polymer chain can also lead to the

decrease in T_g of PNIPAAm.[5] Even so, the two discernable T_gs indicate that these two blocks are incompatible, which may be beneficial for the fabrication of controllable surface wettability.

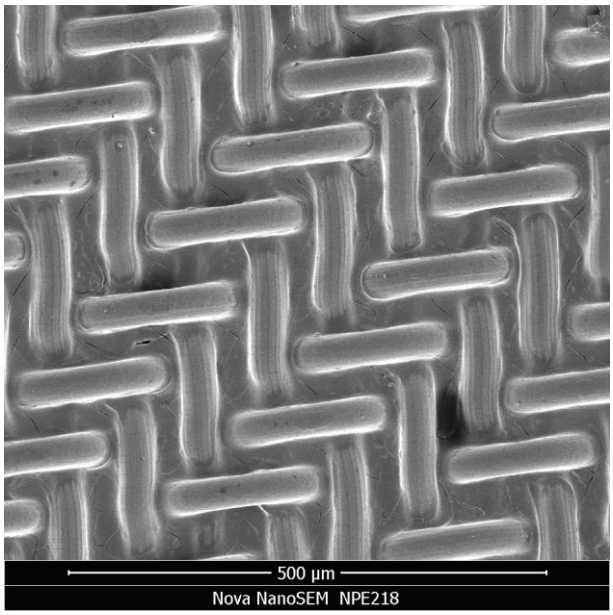

Figure S3. SEM image of the as-prepared film after numerous cycles of the separation processes

Morphology of Film. After a series of separation experiments, the film can maintain its morphology as shown in Figure S3, which indicates that the stability of the film is good in a certain period. This is of great significance in practical application in water/oil separation.

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