Supporting Information

Designing Polyurethane-based Microcapsule with Tailored Swelling Behaviours for Enhanced Oil Recovery

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SI-1: Details of simulation procedure

The simulation procedures are outlined in Figure S1a, involving three distinct steps: compression, circulation, and equilibrium. As depicted in Figure S1b, the density profiles illustrate a gradual convergence of the PU membrane's density with an increasing number of cycles. For model optimization, the same cross-sectional area as the standard was utilized.

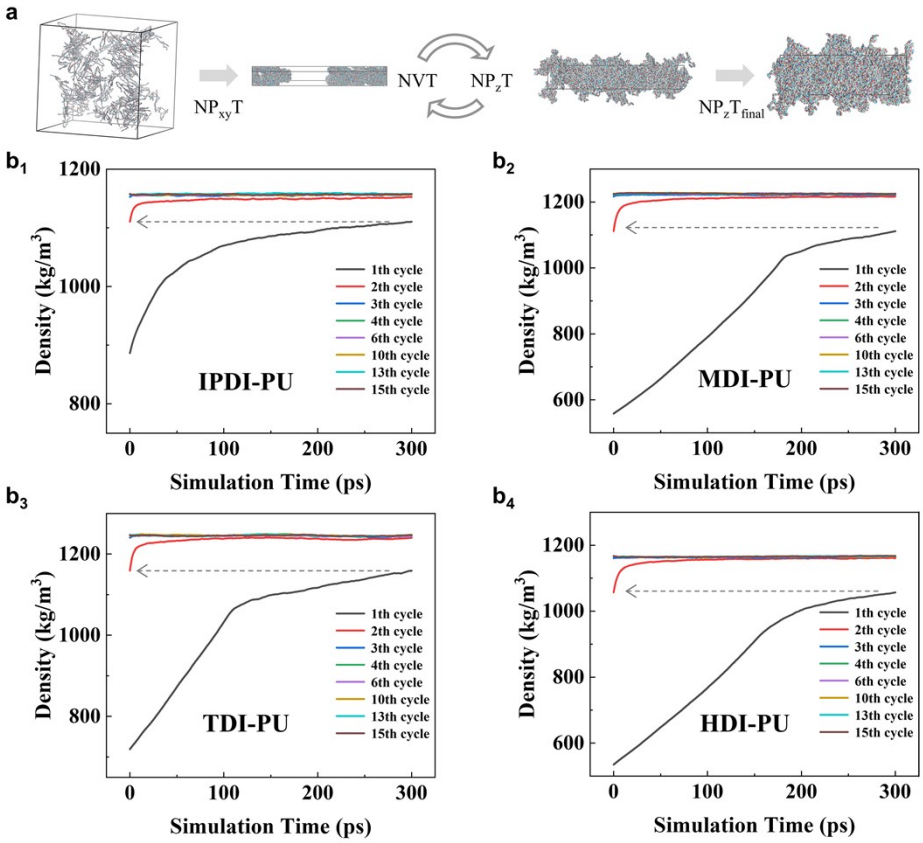

Fig. S1 (a) Snapshot of simulation procedures. (b) Density profiles of four types of PU during 15 compression-relaxation cycles.

SI-2: State of PUs

During simulation, the length of polymer chains was varied between 20 nm and 10 nm. The below figure shows the configuration and end-to-end distance of IPDI-PU before simulation. In reality, the glass transition temperature (Tg) and melting temperature (Tm) of PU-based polymer is closely related to the monomer types, block ratios, and synthesis methods. Specifically, MDI-PU, TDI-PU, and IPDI-PU possess cyclic structures along their chains, resulting in higher rigidity and, consequently, higher Tg and Tm. In contrast, HDI-PU consists of linear chains, leading to relatively lower Tg and Tm. In experiments, the polymers with low degree of polymerization were adopted to achieve controlled release, and that ensures the polymers are in a melt state. In simulations, the polymer chains are relatively shorter than the polymers in experiments. Therefore, in both the experiments and the simulations, the polymers are in a melt state at room temperature.

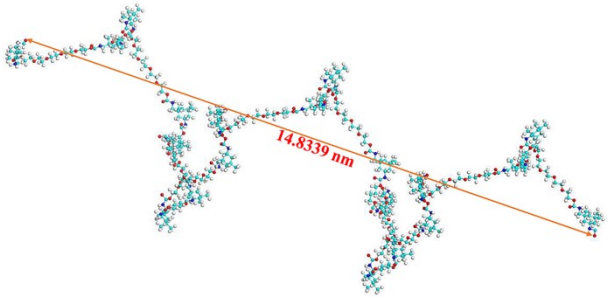

Fig. S2 End-to-end distance of IPDI-PU chain.

SI-3: RMSD analysis

The RMSD profiles demonstrate the equilibrium of PUs. In addition, the RMSD of PUs increases with increasing temperature, as shown in Fig. S3.

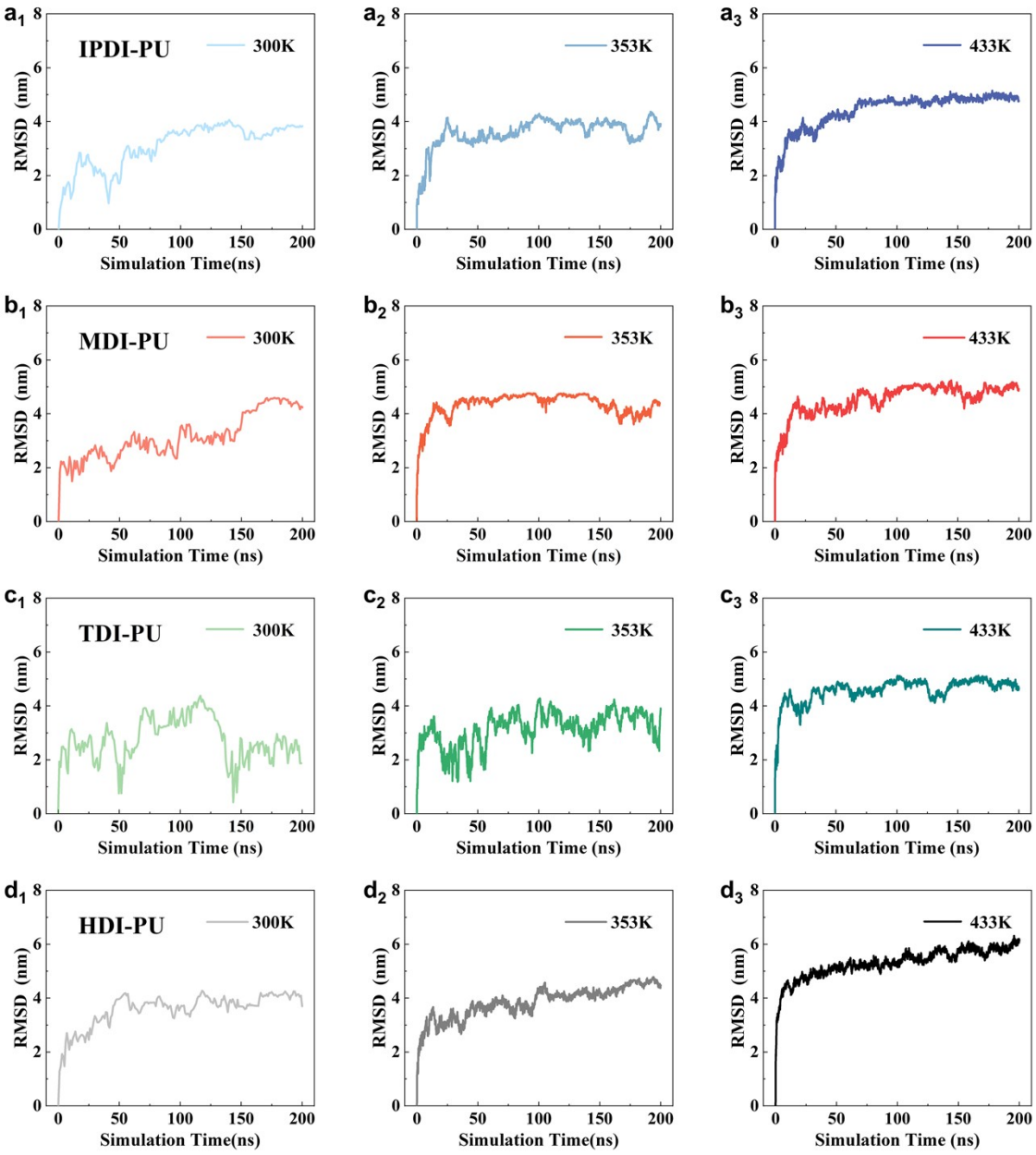

Fig. S3 RMSD profiles of (a) IPDI-PU, (b) MDI-PU, (c) TDI-PU, and (d) HDI-PU at different temperature.

SI-4: MSD analysis

The MSD profiles demonstrate the equilibrium of PUs. The results indicate that, in the initial stages, there was a rapid diffusion process with large curvature. After 50 ns, the MSDs change to linear relationship with simulation time. The results suggest that the polymer systems reach a stable state after about 50 ns, and these results are consistent with density profiles (Fig. 3b). That is, after a rapid diffusion process of water molecules, the water inside membrane is close to the saturated state, thus the density profiles have no significant change after 50 ns.

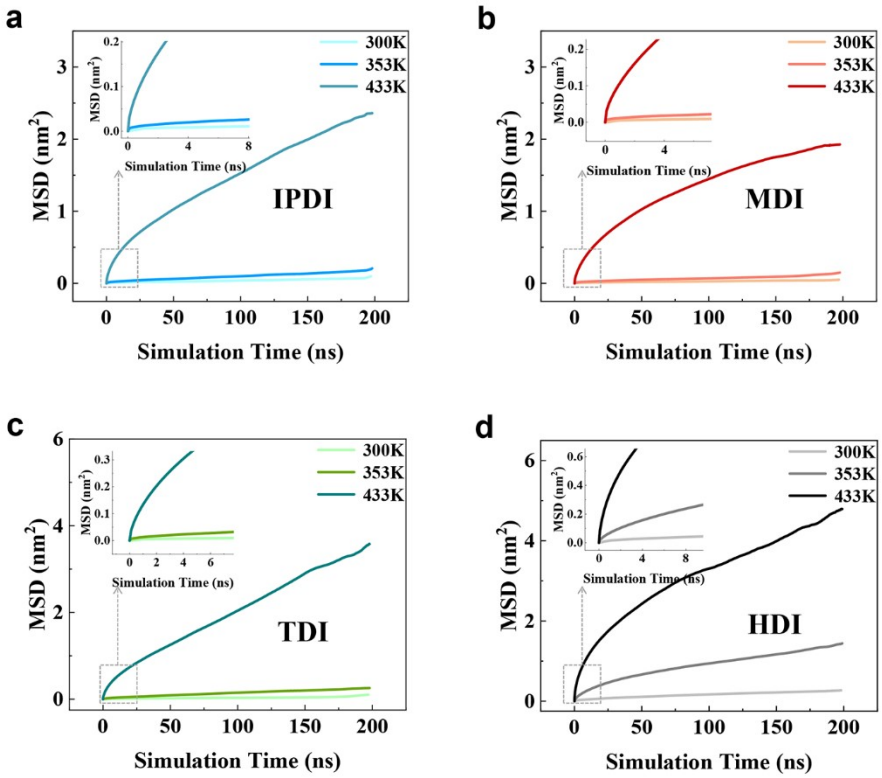

Fig. S4 MSD of (a) IPDI-PU, (b) MDI-PU, (c) TDI-PU, and (d) HDI-PU at different temperatures.

SI-5: Analysis of water molecules

To precisely quantify the count of water molecules within the membrane while mitigating the influence of the water-membrane interface, a region closer to the membrane's interior was selected, as indicated in Fig. S5a. The radial distribution function (RDF) profiles between water molecules and distinct diisocyanate segments indicate that the first peaks are situated around 1.8 Å, as depicted in Fig. S5b. Consequently, a standard of 2 Å was adopted to determine the adsorption of water around various segments.

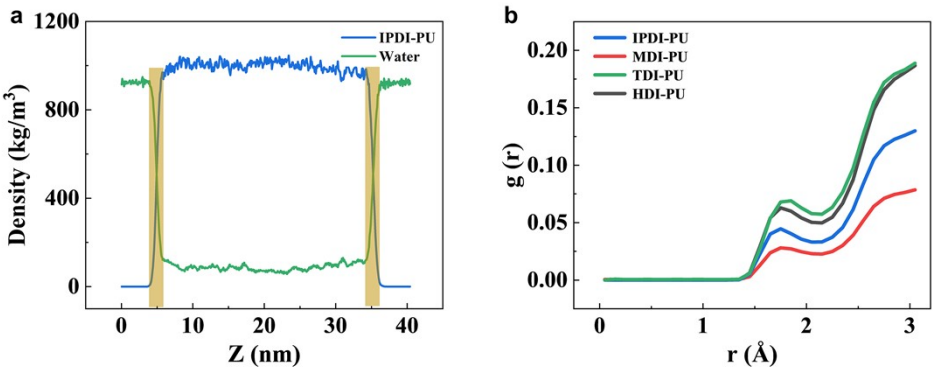

Fig. S5 (a) Density distribution of water and IPDI-PU. (b) Radial distribution functions of water molecules in different diisocyanate segments.

SI-6: Swelling process of membrane

Fig. S6 shows the swelling snapshots of IPDI-PU, MDI-PU, TDI-PU and IPDI-PU at 433 K. It is evident that the PU membrane exhibits significant swelling in the Z-direction.

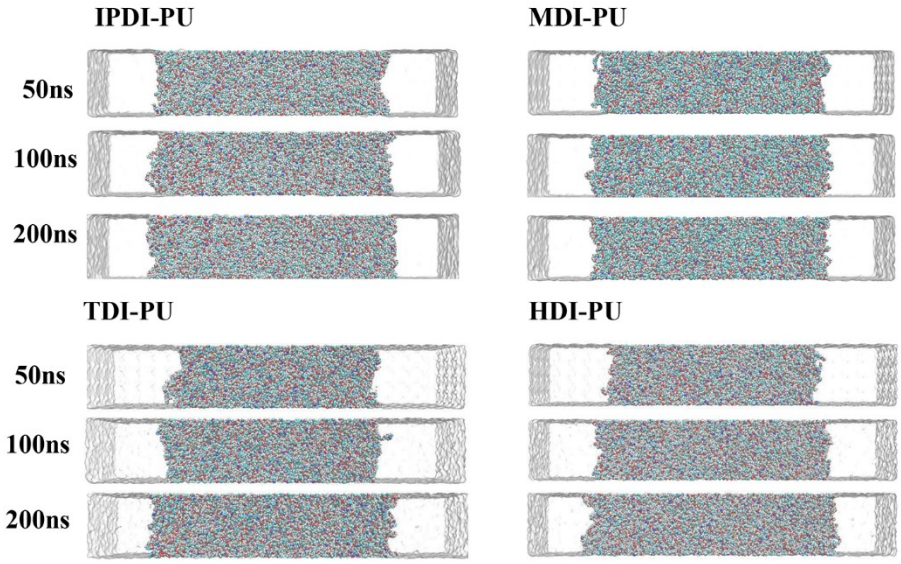

Fig. S6 Snapshots of membrane swelling for IPDI-PU, MDI-PU, TDI-PU and HDI-PU at 433K.

SI-7: Simulation results of four types of PU at 353K

Fig. S7 shows the variation of density of PUs under 353 K.

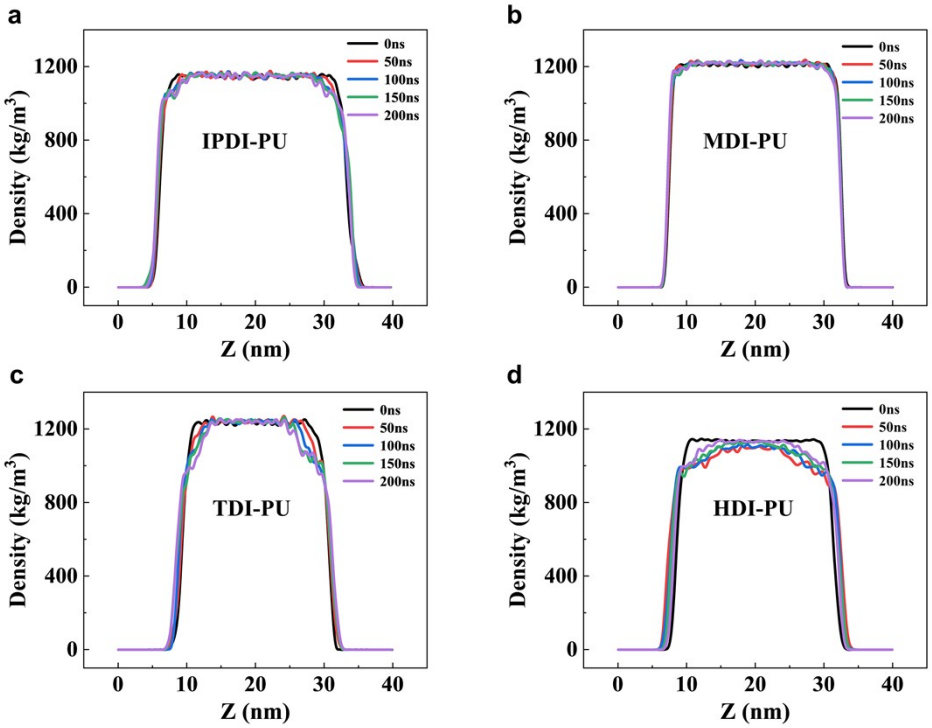

Fig. S7 Density profiles of (a) IPDI-PU, (b) MDI-PU, (c) TDI-PU, and (d) HDI-PU under 353 K.

SI-8: MSD of water

As shown in the Fig. S8, the slope of the MSD of water molecules in all systems increases with rising temperature. The slope of the linear portion between 5 ns and 15 ns is used to calculate the diffusion coefficients (D).

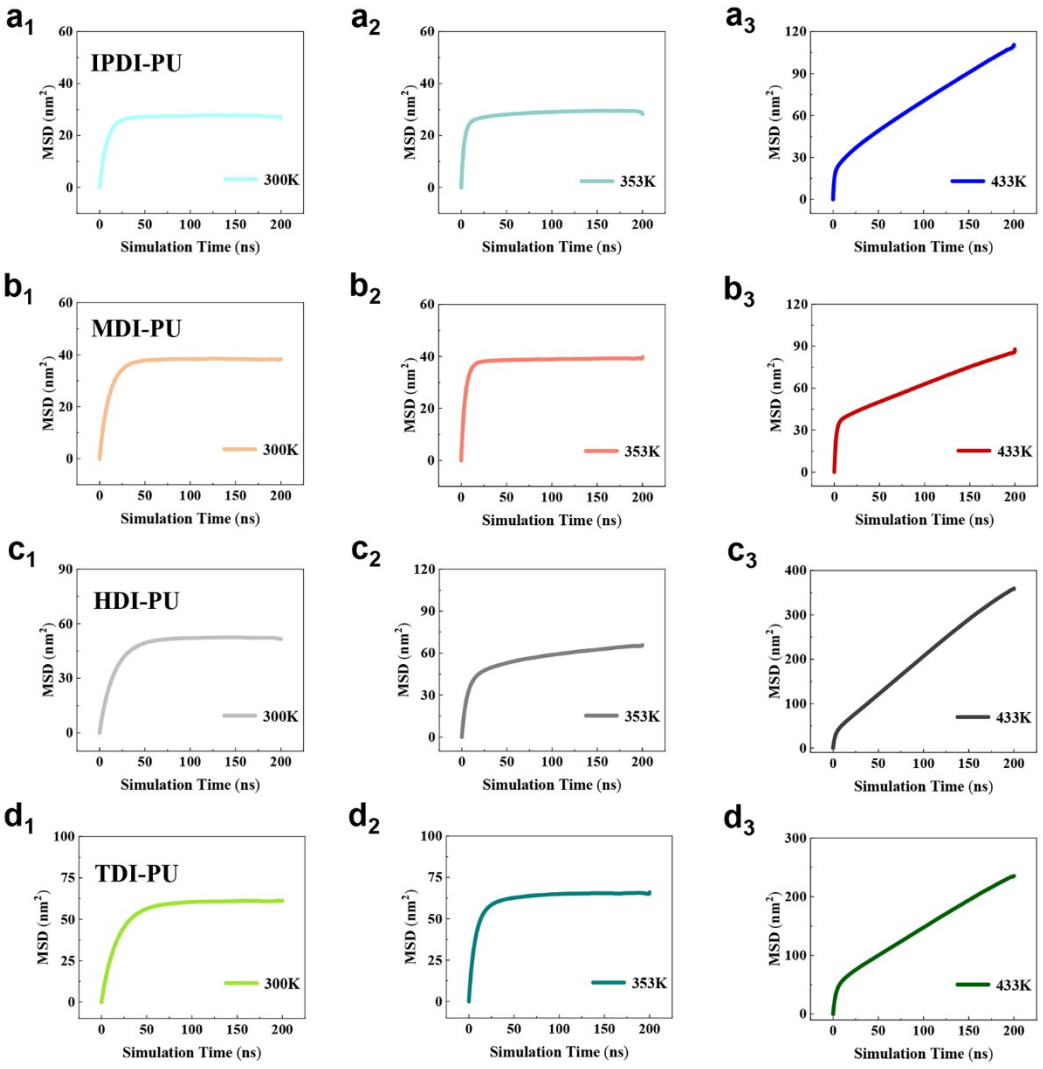

Fig. S8 MSD of water molecules in (a) IPDI-PU, (b) MDI-PU, (c) TDI-PU, and (d) HDI-PU system at different temperatures.

SI-9: Density of water

Fig. S9 shows the density distribution curve of water molecules. The results indicate that, after 200ns of simulation, the density of water molecules follows the changes in membrane swelling. At 50 ns, there is a noticeable increase in water molecule density in the central region of the membrane. However, as the simulation progresses, the density curves of water molecules become less pronounced. After 150 ns, the density curves of water molecules in all four systems essentially overlap, indicating that water has reached an equilibrium state at 433K.

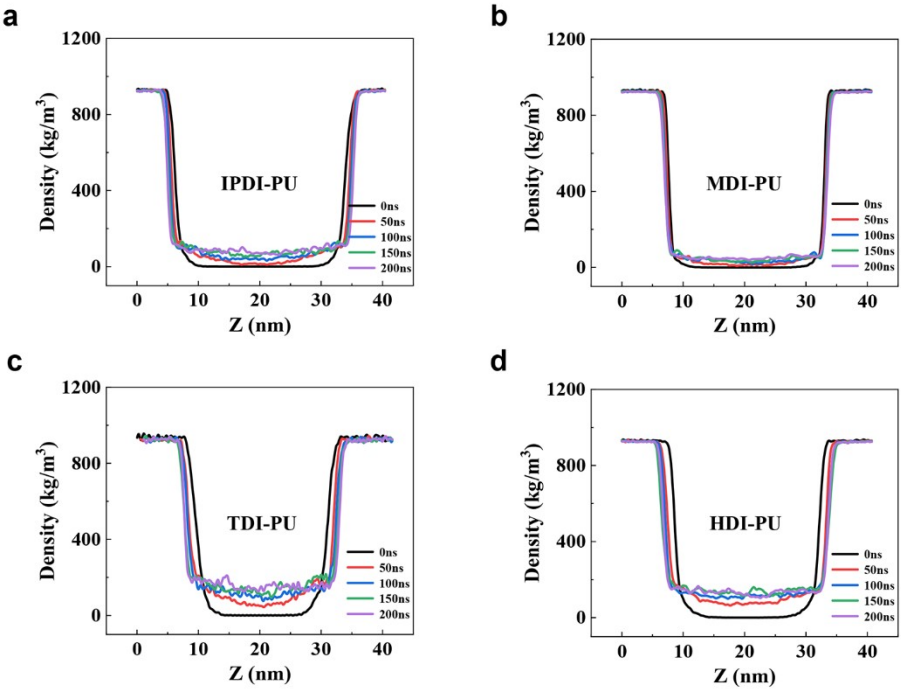

Fig. S9 Water molecule density profiles for (a) IPDI-PU, (b) MDI-PU, (c) TDI-PU, and (d) HDI-PU at 433K.

SI-10: Simulation results of DMPA-PU

Fig. S10a illustrates the variation of density distribution of DMPA-PU under 433 K, and the corresponding simulation snapshots are reported in Fig. S10b.

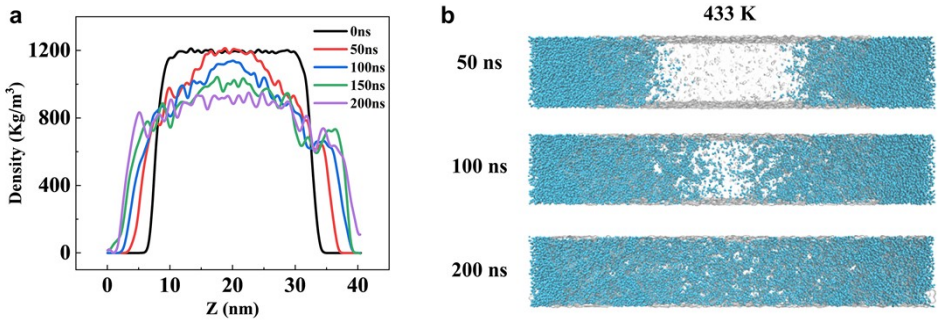

Fig. S10 (a) Variation of density distribution of DMPA-PU under 433 K. (b) Snapshots of system at 50ns, 100ns, and 200ns.