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# Supporting Information

# Cryogenic Efficient Phase Separation of Oil-water Emulsions with Amphiphilic Hyperbranched Poly(amido-amine)

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## I. Materials

Ethylenediamine (EDA) (99 %), methyl acrylate (MA) (98.5 %), palmitic acid (97 %), Tween 80, Span 80, 4-dimethylaminopyridine (DMAP, 99 %) and 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDCI, 98 %) were purchased from Aladdin Chemical Reagent Corporation. Methanol (99.5 %), ethyl ether (99.5 %), chloroform (99 %), acetone (99.5 %), toluene (99.5 %), *n*-hexane (97 %), and triethylamine ($Et_3N$, 99 %) were purchased from Sino-pharm Chemical Reagent

Corporation. Diesel (0#, $\eta_{25\ °C}$ = 5.43 mPa·s; $\rho_{25\ °C}$ = 0.825 g·cm$^{-3}$) was provided by China National Petroleum Corporation. Bitumen samples and various dehydrated crude oils were obtained from Liaohe, Xinan and Xijiang oilfields, China. All of these experiment reagents were used without further purification.

## II. Procedures for Preparation of HPAMAM and CHPAMAM

EDA (15.0 g, 0.25 mol) was dissolved in 50 mL of methanol containing MA (21.5 g, 0.25 mol) with magnetic stirring. The solution was stirred in an ice-water bath for 48 h, and most methanol was removed. Subsequently, the reaction system was kept in an oil bath for 1.5 h at 60 °C to further process the residual methanol. The mixture was reacted at 80 °C, 100 °C, 120 °C and 140 °C for 2 h, respectively, through a rotary evaporator under vacuum to form macromolecules. HPAMAM was purified by precipitating into ethyl ether and dried for 12 h at 50 °C in vacuo.

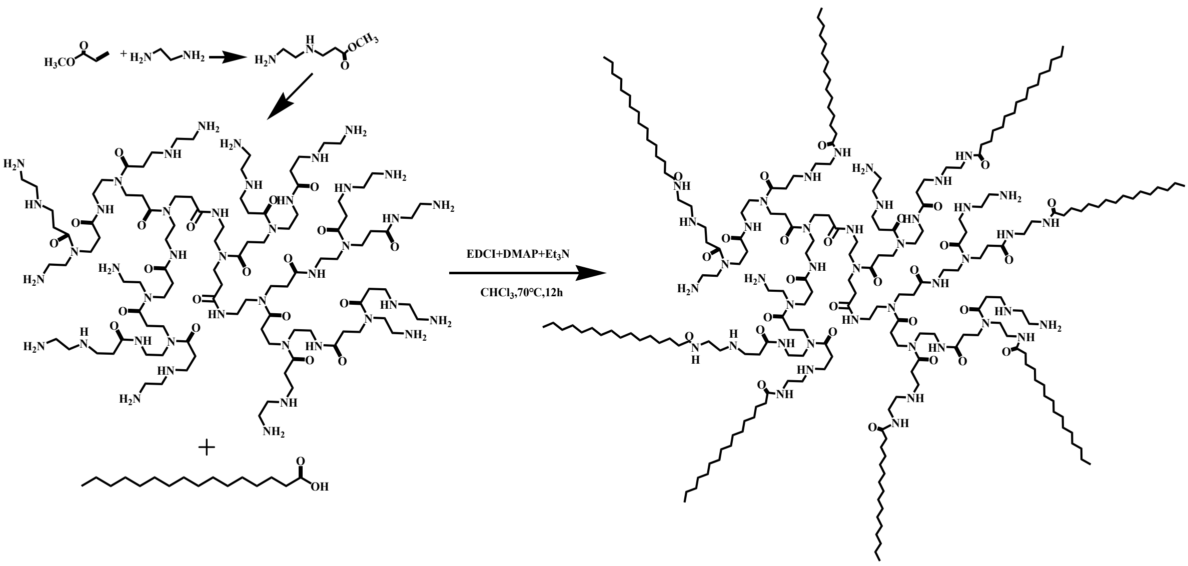


**Fig. S1** Preparation of hyperbranched poly(amido-amine) (HPAMAM) with MA and EDA as starting materials and its functional product CHPAMAM

## III. Preparation of oil-in-water (O/W) simulative emulsions

A series of oil-in-water emulsions were prepared: 10 % w/v diesel and 40 % w/v diesel. For example, 100 g of diesel mixed with 0.18 g of Span 80 was added into a 1000 mL polypropylene beaker containing 1.82 g of Tween 80, and then, water was added to reach the scale mark. Subsequently, the system was deeply stirred at 30000 $r \cdot min^{-1}$ for 15 min with a high-shear mechanical homogenizer (AF-B1, A-FIND, China). The average droplet sizes of two kinds of emulsions measured by dynamic light scattering (DLS) were less than 3 μm, which could ensure the adequate stability of the emulsions during the experimental period.

**IV. Demulsification tests**

The demulsification effect was assessed by measuring the oil removal ratio of emulsions and the water content of the upper phase. In each test, newly formulated emulsions (50 mL) and the demulsifier solution (0.1 mL) with a given concentration were mixed thoroughly by repeated oscillations in a 50 mL color-comparison tube. The emulsions without any demulsifier were compared by applying the same operation conditions as the blank experiment. Subsequently, the colorimetric tubes were placed in a thermostatic water bath (DKZ-2, Shanghai Jinghong, China) to maintain the specified temperature so as to investigate demulsification performance. The residual oil in the lower phase was extracted with *n*-hexane and then its oil content was analyzed by a UV-vis spectrophotometer (Shimadzu, UV-2450, Japan). The oil content was converted into the oil removal ratio of emulsions to indicate the demulsification effect as follows:

$$R = \frac{c_0 - c}{c_0} \times 100\ \% \tag{1}$$

where $R$ (%) is the oil removal ratio of emulsions, $c_0$ ($mg \cdot L^{-1}$) represents the initial oil content of the emulsions, and $c$ (mg·L$^{-1}$) denotes the oil content during the process of demulsification. The wavelength of the characteristic absorption peak of oil, corresponding to $c$ or $c_0$, was at 337.8 nm. Furthermore, the water content of upper phase was determined by Karl Fischer titration with a coulometric KF titrator (C20, Mettler Toledo). To more intuitively monitor the effect of CHPAMAM on demulsification process, the size of droplets in lower emulsion layer after different settling time was observed by an optical microscope.

**V. Interfacial tension correlation**

The dynamic interface tension curves were fitted into a biexponential (four parameter) decay equation to explore the ability of demulsifiers molecules to diffuse, absorb and rearrange on the interface membrane:

$$\gamma = a\mathrm{e}^{(-bt)} + c\mathrm{e}^{(-dt)} \quad (2)$$

where $\gamma$ is the function of oil-water interfacial tension with time, $\gamma_0$ is the initial interfacial tension, $b$ and $d$ represent the decaying trend of oil-water interfacial tension corresponding to the rapid attenuation in the initial stage and the subsequent slow attenuation, respectively. All of the experimental measurements were repeated three times and the average values were taken.

**VI.** *Interfacial film strength measurement*

The single-drop method was implemented to investigate the interfacial film strength and the ability of demulsifier to damage the oil-water interfacial film. The water phase containing the demulsifier and oil phase were placed in a constant temperature water bath. Subsequently, the diesel droplets moved slowly in the water phase to form O/W-type droplets. When emulsified oil droplets reached the stable oil-water interfacial film, timing was triggered. The number of droplets in a single experiment was 50, and the coalescence time of droplets was recorded. Based on the Cockbain theory[34], the rupture rate constant $k$ was calculated with the following equation:

$$\ln\frac{N}{N_0} = kt + \mathrm{c} \tag{3}$$

where $N$ is the number of droplets at the moment $t$, $N_0$ represents the total number of droplets involved in single experiment, and $c$ denotes the regression factor.

The time required for half the number of experimental droplets to rupture is defined as the half-life time of the droplets. The combination of half-life time ($t_{1/2}$), drainage time ($t_\mathrm{d}$), and rupture rate constant ($k$) can be used to evaluate interfacial film strength, and the following relationship is obtained:

$$t_{1/2} = t_\mathrm{d} + \frac{\ln 2}{k} \tag{4}$$

**VII. Interfacial rheology measurement**

Dilatational modulus ($\varepsilon$) is obtained from the ratio of the interfacial tension ($\gamma$) response to the relative area ($A$) variation, as shown in the following equation:

$$\varepsilon = \frac{\mathrm{d}\gamma}{\mathrm{d}\ln A} \tag{5}$$

The dilatational modulus is divided into elastic modulus ($\varepsilon'$) and viscous modulus ($\varepsilon''$). The elastic modulus can effectively reflect the ability of the interfacial film to resist deformation; the viscous modulus is used to predict the diffusion, adsorption and rearrangement ability of the emulsion breaker molecules at the interface. Therefore, dilatational modulus can be drawn as follows:

$$\varepsilon = \varepsilon' + i\varepsilon'' \tag{6}$$

$$\varepsilon'' = \omega\eta_{\mathrm{d}} \tag{7}$$

where $\omega$ and $\eta_d$ are defined as oscillation frequency of the interfacial film and interfacial dilatational viscosity, respectively.

**VIII. Dissipative particle dynamics (DPD) method**

In the DPD simulation, $N_m$ water molecules are typically coarse-grained into a bead. Based on the previous research on the construction of oil-water simulation system, the degree of coarse-grained is set to $N_m$ = 3, indicating that one DPD water bead corresponds to three water molecules in the simulation system of this work. The scales of length ($R_c$), mass ($m$), and time ($\tau$) can be evaluated in terms of the coarse graining:

$$R_{\mathrm{c}} = 3.107(\rho N_{\mathrm{m}})^{1/3}\text{Å} \tag{8}$$

$$m = N_{\mathrm{m}} \cdot m_{\mathrm{water}}\mathrm{amu} \tag{9}$$

$$\tau = (1.41 \pm 0.1)N_{\mathrm{m}}^{5/3}\mathrm{ps} \tag{10}$$

where the reduced density $\rho$ = 3, which denotes the number of beads in a cubic volume of radius $R_c$ is 3; $m_{water}$ is the mass of a water molecule. The above three scales are calculated as $R_c$ = 6.46 Å, $m$ = 54 amu, $\tau$ = 8.8 ps.

The reasonable calculation of the interaction parameters between different structural units is the most critical in DPD simulation to construct the force field of the whole coarse-grained model and explore the motion state of each particle in the system from the mesoscopic level. The DPD theory is correlated with the Flory -

Huggins theory, and the DPD conservative force parameters ($a_{ij}$) are further derived from the Flory-Huggins parameters ($\chi_{ij}$), thus achieving the integration of abstract models and real chemical components, the empirical correlation as follows:

$$a_{ij} \approx a_{ii} + 3.27\chi_{ij}(\rho = 3) \tag{11}$$

where $a_{ii}$ is the repulsive force between homogeneous beads, and $\rho$ is the density of the number of particles in the system. The density $\rho$ of coarse-grained beads is set to 3, therefore the initial $a_{ii}$ is 25, and $a_{ij}$ is 78 in this emulsion system. The parameters $\chi_{ij}$ at different temperatures can be deduced by calculating the solubility parameters of beads $i$ and $j$ in the system:

$$\chi_{ij} = \frac{v_{ij}}{\mathrm{R}T}\left(\delta_i - \delta_j\right)^2 \tag{12}$$

where $v_{ij}$ is the average molar volume of beads $i$ and $j$, $R$ is the ideal gas constant, $\delta_i$ and $\delta_j$ are the Hansen solubility parameters of each bead at temperature $T$. For macromolecular systems where the solubility parameters are difficult to be measured experimentally, the solubility parameters of individual beads in this model are further obtained by Cohesion Energy Density (CED) calculation, as shown in the following equation:

$$\delta_i = \sqrt{\frac{E_{\mathrm{coh}}}{V_i^0}} = \sqrt{\frac{\Delta_{\mathrm{vap}}H_{\mathrm{m}} - \mathrm{R}T}{V_i^0}} \tag{13}$$

where $E_{\mathrm{coh}}$, $V_i^0$ and $\Delta_{\mathrm{vap}}H_{\mathrm{m}}$ are the cohesive energy, volume and enthalpy of vaporization of component $i$, respectively. The calculations are performed with the Forcite module in Materials Studio software.

**Table S1** Volume ($v$) of coarse-grained beads at 303.15 K/ Å$^3$

| 303.15K | $A_2$ | $A_3$ | $A_4$ | $A_6$ | $R_2$ | $R_3$ | $R_4$ | $O_1$ | $O_2$ | S | $N_1$ | $N_2$ | W | PAM | $P_1$ | $P_2$ | $P_3$ | $P_4$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $A_2$ | 58.10 | | | | | | | | | | | | | | | | | |
| $A_3$ | 65.60 | 73.10 | | | | | | | | | | | | | | | | |
| $A_4$ | 73.85 | 81.35 | 89.60 | | | | | | | | | | | | | | | |
| $A_6$ | 73.75 | 81.25 | 89.50 | 89.40 | | | | | | | | | | | | | | |
| $R_2$ | 56.65 | 64.15 | 72.40 | 72.30 | 55.20 | | | | | | | | | | | | | |
| $R_3$ | 66.87 | 74.37 | 82.62 | 82.52 | 65.42 | 75.62 | | | | | | | | | | | | |
| $R_4$ | 76.30 | 83.80 | 92.05 | 91.95 | 74.85 | 85.05 | 94.50 | | | | | | | | | | | |
| $O_1$ | 72.95 | 80.45 | 88.70 | 88.60 | 71.50 | 81.70 | 91.15 | 87.80 | | | | | | | | | | |
| $O_2$ | 58.45 | 65.95 | 74.20 | 74.10 | 57.00 | 67.20 | 76.65 | 73.30 | 58.80 | | | | | | | | | |
| S | 65.60 | 73.10 | 81.35 | 81.25 | 64.15 | 74.35 | 83.80 | 80.45 | 65.95 | 73.10 | | | | | | | | |
| $N_1$ | 71.40 | 78.90 | 87.15 | 87.05 | 69.95 | 80.15 | 89.60 | 86.25 | 71.75 | 78.90 | 84.70 | | | | | | | |
| $N_2$ | 61.65 | 69.15 | 77.40 | 77.30 | 60.20 | 70.40 | 79.85 | 76.50 | 62.00 | 69.15 | 74.95 | 65.20 | | | | | | |
| W | 38.05 | 45.55 | 53.80 | 53.70 | 36.60 | 46.80 | 56.25 | 52.90 | 38.40 | 45.55 | 51.35 | 41.60 | 18.00 | | | | | |
| PAM | 59.79 | 67.29 | 75.54 | 75.44 | 58.34 | 68.54 | 77.99 | 74.64 | 60.14 | 67.29 | 73.09 | 63.34 | 39.74 | 61.49 | | | | |
| $P_1$ | 58.20 | 65.70 | 73.95 | 73.85 | 56.75 | 66.95 | 76.40 | 73.05 | 58.55 | 65.70 | 71.50 | 61.75 | 38.15 | 59.90 | 58.30 | | | |
| $P_2$ | 71.00 | 78.50 | 86.75 | 86.65 | 69.55 | 79.75 | 89.20 | 85.85 | 71.35 | 78.50 | 84.30 | 74.55 | 50.95 | 72.70 | 71.10 | 83.90 | | |
| $P_3$ | 53.40 | 60.90 | 69.15 | 69.05 | 51.95 | 62.15 | 71.60 | 68.25 | 53.75 | 60.90 | 66.70 | 56.95 | 33.35 | 55.10 | 53.50 | 66.30 | 48.70 | |
| $P_4$ | 95.80 | 103.30 | 111.55 | 111.45 | 94.35 | 104.55 | 114.00 | 110.65 | 96.15 | 103.30 | 109.10 | 99.35 | 75.75 | 97.50 | 95.90 | 108.70 | 91.10 | 133.50 |

**Table S2** Volume ($v$) of coarse-grained beads at 318.15 K/ Å$^3$

| 318.15K | $A_2$ | $A_3$ | $A_4$ | $A_6$ | $R_2$ | $R_3$ | $R_4$ | $O_1$ | $O_2$ | S | $N_1$ | $N_2$ | W | PAM | $P_1$ | $P_2$ | $P_3$ | $P_4$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $A_2$ | 58.10 | | | | | | | | | | | | | | | | | |
| $A_3$ | 65.60 | 73.10 | | | | | | | | | | | | | | | | |
| $A_4$ | 73.85 | 81.35 | 89.60 | | | | | | | | | | | | | | | |
| $A_6$ | 73.75 | 81.25 | 89.50 | 89.40 | | | | | | | | | | | | | | |
| $R_2$ | 56.65 | 64.15 | 72.40 | 72.30 | 55.20 | | | | | | | | | | | | | |
| $R_3$ | 66.87 | 74.37 | 82.62 | 82.52 | 65.42 | 75.62 | | | | | | | | | | | | |
| $R_4$ | 76.30 | 83.80 | 92.05 | 91.95 | 74.85 | 85.05 | 94.50 | | | | | | | | | | | |
| $O_1$ | 72.95 | 80.45 | 88.70 | 88.60 | 71.50 | 81.70 | 91.15 | 87.80 | | | | | | | | | | |
| $O_2$ | 58.45 | 65.95 | 74.20 | 74.10 | 57.00 | 67.20 | 76.65 | 73.30 | 58.80 | | | | | | | | | |
| S | 65.60 | 73.10 | 81.35 | 81.25 | 64.15 | 74.35 | 83.80 | 80.45 | 65.95 | 73.10 | | | | | | | | |
| $N_1$ | 71.40 | 78.90 | 87.15 | 87.05 | 69.95 | 80.15 | 89.60 | 86.25 | 71.75 | 78.90 | 84.70 | | | | | | | |
| $N_2$ | 61.65 | 69.15 | 77.40 | 77.30 | 60.20 | 70.40 | 79.85 | 76.50 | 62.00 | 69.15 | 74.95 | 65.20 | | | | | | |
| W | 38.05 | 45.55 | 53.80 | 53.70 | 36.60 | 46.80 | 56.25 | 52.90 | 38.40 | 45.55 | 51.35 | 41.60 | 18.00 | | | | | |
| PAM | 59.79 | 67.29 | 75.54 | 75.44 | 58.34 | 68.54 | 77.99 | 74.64 | 60.14 | 67.29 | 73.09 | 63.34 | 39.74 | 61.49 | | | | |
| $P_1$ | 58.20 | 65.70 | 73.95 | 73.85 | 56.75 | 66.95 | 76.40 | 73.05 | 58.55 | 65.70 | 71.50 | 61.75 | 38.15 | 59.90 | 58.30 | | | |

| | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **$P_2$** | 71.00 | 78.50 | 86.75 | 86.65 | 69.55 | 79.75 | 89.20 | 85.85 | 71.35 | 78.50 | 84.30 | 74.55 | 50.95 | 72.70 | 71.10 | 83.90 | | |
| **$P_3$** | 53.40 | 60.90 | 69.15 | 69.05 | 51.95 | 62.15 | 71.60 | 68.25 | 53.75 | 60.90 | 66.70 | 56.95 | 33.35 | 55.10 | 53.50 | 66.30 | 48.70 | |
| **$P_4$** | 95.80 | 103.30 | 111.55 | 111.45 | 94.35 | 104.55 | 114.00 | 110.65 | 96.15 | 103.30 | 109.10 | 99.35 | 75.75 | 97.50 | 95.90 | 108.70 | 91.10 | 133.50 |

**Table S3** Volume ($v$) of coarse-grained beads at 333.15 K/ Å$^3$

| **333.15K** | **$A_2$** | **$A_3$** | **$A_4$** | **$A_6$** | **$R_2$** | **$R_3$** | **$R_4$** | **$O_1$** | **$O_2$** | **S** | **$N_1$** | **$N_2$** | **W** | **PAM** | **$P_1$** | **$P_2$** | **$P_3$** | **$P_4$** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **$A_2$** | 58.10 | | | | | | | | | | | | | | | | | |
| **$A_3$** | 65.60 | 73.10 | | | | | | | | | | | | | | | | |
| **$A_4$** | 73.85 | 81.35 | 89.60 | | | | | | | | | | | | | | | |
| **$A_6$** | 73.75 | 81.25 | 89.50 | 89.40 | | | | | | | | | | | | | | |
| **$R_2$** | 56.65 | 64.15 | 72.40 | 72.30 | 55.20 | | | | | | | | | | | | | |
| **$R_3$** | 66.87 | 74.37 | 82.62 | 82.52 | 65.42 | 75.62 | | | | | | | | | | | | |
| **$R_4$** | 76.30 | 83.80 | 92.05 | 91.95 | 74.85 | 85.05 | 94.50 | | | | | | | | | | | |
| **$O_1$** | 72.95 | 80.45 | 88.70 | 88.60 | 71.50 | 81.70 | 91.15 | 87.80 | | | | | | | | | | |
| **$O_2$** | 58.45 | 65.95 | 74.20 | 74.10 | 57.00 | 67.20 | 76.65 | 73.30 | 58.80 | | | | | | | | | |
| **S** | 65.60 | 73.10 | 81.35 | 81.25 | 64.15 | 74.35 | 83.80 | 80.45 | 65.95 | 73.10 | | | | | | | | |
| **$N_1$** | 71.40 | 78.90 | 87.15 | 87.05 | 69.95 | 80.15 | 89.60 | 86.25 | 71.75 | 78.90 | 84.70 | | | | | | | |
| **$N_2$** | 61.65 | 69.15 | 77.40 | 77.30 | 60.20 | 70.40 | 79.85 | 76.50 | 62.00 | 69.15 | 74.95 | 65.20 | | | | | | |
| **W** | 38.05 | 45.55 | 53.80 | 53.70 | 36.60 | 46.80 | 56.25 | 52.90 | 38.40 | 45.55 | 51.35 | 41.60 | 18.00 | | | | | |
| **PAM** | 59.79 | 67.29 | 75.54 | 75.44 | 58.34 | 68.54 | 77.99 | 74.64 | 60.14 | 67.29 | 73.09 | 63.34 | 39.74 | 61.49 | | | | |
| **$P_1$** | 58.20 | 65.70 | 73.95 | 73.85 | 56.75 | 66.95 | 76.40 | 73.05 | 58.55 | 65.70 | 71.50 | 61.75 | 38.15 | 59.90 | 58.30 | | | |
| **$P_2$** | 71.00 | 78.50 | 86.75 | 86.65 | 69.55 | 79.75 | 89.20 | 85.85 | 71.35 | 78.50 | 84.30 | 74.55 | 50.95 | 72.70 | 71.10 | 83.90 | | |
| **$P_3$** | 53.40 | 60.90 | 69.15 | 69.05 | 51.95 | 62.15 | 71.60 | 68.25 | 53.75 | 60.90 | 66.70 | 56.95 | 33.35 | 55.10 | 53.50 | 66.30 | 48.70 | |
| **$P_4$** | 95.80 | 103.30 | 111.55 | 111.45 | 94.35 | 104.55 | 114.00 | 110.65 | 96.15 | 103.30 | 109.10 | 99.35 | 75.75 | 97.50 | 95.90 | 108.70 | 91.10 | 133.50 |

**Table S4** Solubility parameter ($\delta$) of coarse-grained beads at 303.15 K/ MPa$^{1/2}$

| **303.15K** | **$A_2$** | **$A_3$** | **$A_4$** | **$A_6$** | **$R_2$** | **$R_3$** | **$R_4$** | **$O_1$** | **$O_2$** | **S** | **$N_1$** | **$N_2$** | **W** | **PAM** | **$P_1$** | **$P_2$** | **$P_3$** | **$P_4$** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **$A_2$** | 0.00 | | | | | | | | | | | | | | | | | |
| **$A_3$** | 6.02 | 0.00 | | | | | | | | | | | | | | | | |
| **$A_4$** | 11.99 | 1.02 | 0.00 | | | | | | | | | | | | | | | |
| **$A_6$** | 17.91 | 3.16 | 0.59 | 0.00 | | | | | | | | | | | | | | |
| **$R_2$** | 0.38 | 9.42 | 16.63 | 23.50 | 0.00 | | | | | | | | | | | | | |
| **$R_3$** | 0.03 | 5.15 | 10.75 | 16.38 | 0.64 | 0.00 | | | | | | | | | | | | |
| **$R_4$** | 0.71 | 2.59 | 6.86 | 11.48 | 2.13 | 0.44 | 0.00 | | | | | | | | | | | |
| **$O_1$** | 54.33 | 24.18 | 15.27 | 9.85 | 63.79 | 51.64 | 42.59 | 0.00 | | | | | | | | | | |
| **$O_2$** | 72.89 | 37.01 | 25.75 | 18.53 | 83.78 | 69.77 | 59.18 | 1.36 | 0.00 | | | | | | | | | |
| **S** | 24.78 | 6.37 | 2.29 | 0.56 | 31.28 | 22.97 | 17.08 | 5.73 | 12.67 | 0.00 | | | | | | | | |
| **$N_1$** | 42.47 | 16.51 | 9.33 | 5.22 | 50.88 | 40.10 | 32.18 | 0.73 | 4.08 | 2.37 | 0.00 | | | | | | | |
| **$N_2$** | 20.04 | 4.09 | 1.03 | 0.06 | 25.93 | 18.42 | 13.19 | 8.38 | 16.49 | 0.25 | 4.16 | 0.00 | | | | | | |
| **W** | 1053.33 | 900.09 | 840.56 | 796.52 | 1093.68 | 1041.38 | 999.23 | 629.22 | 572.05 | 755.01 | 672.77 | 782.79 | 0.00 | | | | | |
| **PAM** | 165.76 | 108.61 | 88.59 | 74.69 | 182.00 | 161.04 | 144.73 | 30.30 | 18.81 | 62.37 | 40.42 | 70.53 | 383.38 | 0.00 | | | | |

| | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **$P_1$** | 3.72 | 0.27 | 2.35 | 5.30 | 6.48 | 3.05 | 1.18 | 29.60 | 43.66 | 9.29 | 21.04 | 6.49 | 931.78 | 119.79 | 0.00 | | | |
| **$P_2$** | 145.49 | 92.32 | 73.95 | 61.30 | 160.73 | 141.07 | 125.84 | 22.01 | 12.42 | 50.19 | 30.75 | 57.54 | 415.87 | 0.66 | 102.66 | 0.00 | | |
| **$P_3$** | 91.84 | 50.84 | 37.46 | 28.63 | 104.02 | 88.34 | 76.37 | 4.90 | 1.09 | 21.21 | 9.40 | 26.08 | 523.11 | 10.83 | 58.58 | 6.14 | 0.00 | |
| **$P_4$** | 50.92 | 21.92 | 13.49 | 8.43 | 60.08 | 48.32 | 39.58 | 0.06 | 1.97 | 4.66 | 0.38 | 7.07 | 641.08 | 32.94 | 27.10 | 24.27 | 5.99 | 0.00 |

**Table S5** Solubility parameter ($\delta$) of coarse-grained beads at 318.15 K/ $MPa^{1/2}$

| **318.15K** | **$A_2$** | **$A_3$** | **$A_4$** | **$A_6$** | **$R_2$** | **$R_3$** | **$R_4$** | **$O_1$** | **$O_2$** | **S** | **$N_1$** | **$N_2$** | **W** | **PAM** | **$P_1$** | **$P_2$** | **$P_3$** | **$P_4$** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **$A_2$** | 0.00 | | | | | | | | | | | | | | | | | |
| **$A_3$** | 6.64 | 0.00 | | | | | | | | | | | | | | | | |
| **$A_4$** | 13.81 | 1.30 | 0.00 | | | | | | | | | | | | | | | |
| **$A_6$** | 20.23 | 3.69 | 0.61 | 0.00 | | | | | | | | | | | | | | |
| **$R_2$** | 0.22 | 9.28 | 17.52 | 24.67 | 0.00 | | | | | | | | | | | | | |
| **$R_3$** | 0.33 | 4.01 | 9.87 | 15.39 | 1.09 | 0.00 | | | | | | | | | | | | |
| **$R_4$** | 1.17 | 2.23 | 6.94 | 11.66 | 2.41 | 0.26 | 0.00 | | | | | | | | | | | |
| **$O_1$** | 60.94 | 27.35 | 16.72 | 10.95 | 68.48 | 52.30 | 45.20 | 0.00 | | | | | | | | | | |
| **$O_2$** | 75.19 | 37.14 | 24.54 | 17.41 | 83.53 | 65.55 | 57.57 | 0.75 | 0.00 | | | | | | | | | |
| **S** | 27.10 | 6.91 | 2.22 | 0.50 | 32.20 | 21.45 | 17.00 | 6.76 | 12.01 | 0.00 | | | | | | | | |
| **$N_1$** | 43.86 | 16.37 | 8.44 | 4.51 | 50.28 | 36.57 | 30.68 | 1.40 | 4.20 | 2.01 | 0.00 | | | | | | | |
| **$N_2$** | 20.84 | 3.95 | 0.72 | 0.00 | 25.33 | 15.92 | 12.12 | 10.51 | 16.86 | 0.41 | 4.23 | 0.00 | | | | | | |
| **W** | 1034.02 | 874.93 | 808.78 | 764.98 | 1064.37 | 997.38 | 965.53 | 592.91 | 551.55 | 726.31 | 651.97 | 761.29 | 0.00 | | | | | |
| **PAM** | 168.52 | 108.26 | 85.83 | 71.97 | 180.91 | 153.93 | 141.57 | 26.78 | 18.58 | 60.46 | 40.44 | 70.85 | 367.66 | 0.00 | | | | |
| **$P_1$** | 4.76 | 0.16 | 2.36 | 5.37 | 7.02 | 2.58 | 1.21 | 31.64 | 42.12 | 9.15 | 19.72 | 5.68 | 898.49 | 116.65 | 0.00 | | | |
| **$P_2$** | 152.63 | 95.60 | 74.60 | 61.72 | 164.42 | 138.75 | 127.04 | 20.68 | 13.57 | 51.10 | 32.85 | 60.68 | 392.12 | 0.39 | 103.49 | 0.00 | | |
| **$P_3$** | 92.57 | 49.62 | 34.86 | 26.25 | 101.81 | 81.84 | 72.90 | 3.29 | 0.90 | 19.49 | 8.99 | 25.57 | 507.82 | 11.29 | 55.35 | 7.47 | 0.00 | |
| **$P_4$** | 55.07 | 23.47 | 13.72 | 8.55 | 62.25 | 46.87 | 40.17 | 0.15 | 1.56 | 4.91 | 0.64 | 8.16 | 611.82 | 30.92 | 27.46 | 24.33 | 4.84 | 0.00 |

**Table S6** Solubility parameter ($\delta$) of coarse-grained beads at 333.15 K/ $MPa^{1/2}$

| **333.15K** | **$A_2$** | **$A_3$** | **$A_4$** | **$A_6$** | **$R_2$** | **$R_3$** | **$R_4$** | **$O_1$** | **$O_2$** | **S** | **$N_1$** | **$N_2$** | **W** | **PAM** | **$P_1$** | **$P_2$** | **$P_3$** | **$P_4$** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **$A_2$** | 0.00 | | | | | | | | | | | | | | | | | |
| **$A_3$** | 7.03 | 0.00 | | | | | | | | | | | | | | | | |
| **$A_4$** | 15.94 | 1.80 | 0.00 | | | | | | | | | | | | | | | |
| **$A_6$** | 23.68 | 4.91 | 0.76 | 0.00 | | | | | | | | | | | | | | |
| **$R_2$** | 0.02 | 6.26 | 14.77 | 22.24 | 0.00 | | | | | | | | | | | | | |
| **$R_3$** | 2.02 | 1.52 | 6.62 | 11.87 | 1.61 | 0.00 | | | | | | | | | | | | |
| **$R_4$** | 2.81 | 0.95 | 5.37 | 10.18 | 2.33 | 0.07 | 0.00 | | | | | | | | | | | |
| **$O_1$** | 64.05 | 28.64 | 16.08 | 9.84 | 61.67 | 43.34 | 40.03 | 0.00 | | | | | | | | | | |
| **$O_2$** | 73.98 | 35.40 | 21.23 | 13.95 | 71.42 | 51.57 | 47.96 | 0.36 | 0.00 | | | | | | | | | |
| **S** | 31.38 | 8.71 | 2.59 | 0.54 | 29.72 | 17.49 | 15.41 | 5.76 | 8.99 | 0.00 | | | | | | | | |
| **$N_1$** | 52.01 | 20.80 | 10.36 | 5.50 | 49.87 | 33.55 | 30.65 | 0.63 | 1.93 | 2.59 | 0.00 | | | | | | | |
| **$N_2$** | 23.15 | 4.67 | 0.67 | 0.00 | 21.72 | 11.50 | 9.83 | 10.19 | 14.36 | 0.63 | 5.76 | 0.00 | | | | | | |
| **W** | 1093.96 | 925.62 | 845.76 | 795.75 | 1084.06 | 1002.04 | 985.90 | 628.61 | 598.98 | 754.77 | 668.89 | 798.85 | 0.00 | | | | | |

| | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **PAM** | 180.77 | 116.51 | 89.34 | 73.60 | 176.76 | 144.60 | 138.51 | 29.62 | 23.46 | 61.51 | 38.85 | 74.55 | 385.34 | 0.00 | | | | |
| **$P_1$** | 2.84 | 18.80 | 32.24 | 42.91 | 3.37 | 9.64 | 11.29 | 93.85 | 105.80 | 53.10 | 79.15 | 42.19 | 1208.24 | 228.91 | 0.00 | | | |
| **$P_2$** | 81.87 | 40.92 | 25.55 | 17.49 | 79.17 | 58.19 | 54.35 | 1.09 | 0.20 | 11.87 | 3.37 | 17.95 | 577.30 | 19.33 | 115.20 | 0.00 | | |
| **$P_3$** | 16.67 | 2.05 | 0.01 | 0.61 | 15.47 | 7.09 | 5.80 | 15.36 | 20.41 | 2.31 | 9.79 | 0.53 | 840.51 | 87.64 | 33.27 | 24.65 | 0.00 | |
| **$P_4$** | 18.60 | 2.76 | 0.10 | 0.31 | 17.33 | 8.37 | 6.95 | 13.62 | 18.39 | 1.66 | 8.40 | 0.25 | 827.25 | 83.39 | 35.98 | 22.42 | 0.05 | 0.00 |

**Table S7** Flory-Huggins parameter ($\chi_{ij}$) of coarse-grained beads at 303.15 K

| **303.15K** | **$A_2$** | **$A_3$** | **$A_4$** | **$A_6$** | **$R_2$** | **$R_3$** | **$R_4$** | **$O_1$** | **$O_2$** | **S** | **$N_1$** | **$N_2$** | **W** | **PAM** | **$P_1$** | **$P_2$** | **$P_3$** | **$P_4$** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **$A_2$** | 0.00 | | | | | | | | | | | | | | | | | |
| **$A_3$** | 0.16 | 0.00 | | | | | | | | | | | | | | | | |
| **$A_4$** | 0.35 | 0.03 | 0.00 | | | | | | | | | | | | | | | |
| **$A_6$** | 0.52 | 0.10 | 0.02 | 0.00 | | | | | | | | | | | | | | |
| **$R_2$** | 0.01 | 0.24 | 0.48 | 0.67 | 0.00 | | | | | | | | | | | | | |
| **$R_3$** | 0.00 | 0.15 | 0.35 | 0.54 | 0.02 | 0.00 | | | | | | | | | | | | |
| **$R_4$** | 0.02 | 0.09 | 0.25 | 0.42 | 0.06 | 0.01 | 0.00 | | | | | | | | | | | |
| **$O_1$** | 1.57 | 0.77 | 0.54 | 0.35 | 1.81 | 1.67 | 1.54 | 0.00 | | | | | | | | | | |
| **$O_2$** | 1.69 | 0.97 | 0.76 | 0.54 | 1.89 | 1.86 | 1.80 | 0.04 | 0.00 | | | | | | | | | |
| **S** | 0.64 | 0.18 | 0.07 | 0.02 | 0.80 | 0.68 | 0.57 | 0.18 | 0.33 | 0.00 | | | | | | | | |
| **$N_1$** | 1.20 | 0.52 | 0.32 | 0.18 | 1.41 | 1.28 | 1.14 | 0.02 | 0.12 | 0.07 | 0.00 | | | | | | | |
| **$N_2$** | 0.49 | 0.11 | 0.03 | 0.00 | 0.62 | 0.51 | 0.42 | 0.25 | 0.41 | 0.01 | 0.12 | 0.00 | | | | | | |
| **W** | 15.90 | 16.27 | 17.94 | 16.97 | 15.88 | 19.34 | 22.30 | 13.21 | 8.72 | 13.65 | 13.71 | 12.92 | 0.00 | | | | | |
| **PAM** | 3.93 | 2.90 | 2.66 | 2.24 | 4.21 | 4.38 | 4.48 | 0.90 | 0.45 | 1.67 | 1.17 | 1.77 | 6.04 | 0.00 | | | | |
| **$P_1$** | 0.09 | 0.01 | 0.07 | 0.16 | 0.15 | 0.08 | 0.04 | 0.86 | 1.01 | 0.24 | 0.60 | 0.16 | 14.10 | 2.85 | 0.00 | | | |
| **$P_2$** | 4.10 | 2.88 | 2.55 | 2.11 | 4.44 | 4.46 | 4.45 | 0.75 | 0.35 | 1.56 | 1.03 | 1.70 | 8.41 | 0.02 | 2.90 | 0.00 | | |
| **$P_3$** | 1.95 | 1.23 | 1.03 | 0.78 | 2.14 | 2.18 | 2.17 | 0.13 | 0.02 | 0.51 | 0.25 | 0.59 | 6.92 | 0.24 | 1.24 | 0.16 | 0.00 | |
| **$P_4$** | 1.94 | 0.90 | 0.60 | 0.37 | 2.25 | 2.00 | 1.79 | 0.00 | 0.07 | 0.19 | 0.02 | 0.28 | 19.27 | 1.27 | 1.03 | 1.05 | 0.22 | 0.00 |

**Table S8** Flory-Huggins parameter ($\chi_{ij}$) of coarse-grained beads at 318.15 K

| **318.15K** | **$A_2$** | **$A_3$** | **$A_4$** | **$A_6$** | **$R_2$** | **$R_3$** | **$R_4$** | **$O_1$** | **$O_2$** | **S** | **$N_1$** | **$N_2$** | **W** | **PAM** | **$P_1$** | **$P_2$** | **$P_3$** | **$P_4$** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **$A_2$** | 0.00 | | | | | | | | | | | | | | | | | |
| **$A_3$** | 0.17 | 0.00 | | | | | | | | | | | | | | | | |
| **$A_4$** | 0.40 | 0.04 | 0.00 | | | | | | | | | | | | | | | |
| **$A_6$** | 0.59 | 0.12 | 0.02 | 0.00 | | | | | | | | | | | | | | |
| **$R_2$** | 0.00 | 0.24 | 0.50 | 0.71 | 0.00 | | | | | | | | | | | | | |
| **$R_3$** | 0.01 | 0.12 | 0.32 | 0.50 | 0.03 | 0.00 | | | | | | | | | | | | |
| **$R_4$** | 0.04 | 0.07 | 0.25 | 0.43 | 0.07 | 0.01 | 0.00 | | | | | | | | | | | |
| **$O_1$** | 1.76 | 0.87 | 0.59 | 0.38 | 1.94 | 1.70 | 1.63 | 0.00 | | | | | | | | | | |
| **$O_2$** | 1.74 | 0.97 | 0.72 | 0.51 | 1.89 | 1.75 | 1.75 | 0.02 | 0.00 | | | | | | | | | |
| **S** | 0.71 | 0.20 | 0.07 | 0.02 | 0.82 | 0.63 | 0.57 | 0.22 | 0.31 | 0.00 | | | | | | | | |
| **$N_1$** | 1.24 | 0.51 | 0.29 | 0.16 | 1.40 | 1.16 | 1.09 | 0.05 | 0.12 | 0.06 | 0.00 | | | | | | | |
| **$N_2$** | 0.51 | 0.11 | 0.02 | 0.00 | 0.61 | 0.44 | 0.38 | 0.32 | 0.41 | 0.01 | 0.13 | 0.00 | | | | | | |

| | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **W** | 15.61 | 15.81 | 17.26 | 16.30 | 15.46 | 18.52 | 21.55 | 12.44 | 8.40 | 13.13 | 13.28 | 12.57 | 0.00 | | | | | |
| **PAM** | 4.00 | 2.89 | 2.57 | 2.15 | 4.19 | 4.19 | 4.38 | 0.79 | 0.44 | 1.61 | 1.17 | 1.78 | 5.80 | 0.00 | | | | |
| **$P_1$** | 0.11 | 0.00 | 0.07 | 0.16 | 0.16 | 0.07 | 0.04 | 0.92 | 0.98 | 0.24 | 0.56 | 0.14 | 13.60 | 2.77 | 0.00 | | | |
| **$P_2$** | 4.30 | 2.98 | 2.57 | 2.12 | 4.54 | 4.39 | 4.50 | 0.70 | 0.38 | 1.59 | 1.10 | 1.79 | 7.93 | 0.01 | 2.92 | 0.00 | | |
| **$P_3$** | 1.96 | 1.20 | 0.96 | 0.72 | 2.10 | 2.02 | 2.07 | 0.09 | 0.02 | 0.47 | 0.24 | 0.58 | 6.72 | 0.25 | 1.17 | 0.20 | 0.00 | |
| **$P_4$** | 2.09 | 0.96 | 0.61 | 0.38 | 2.33 | 1.94 | 1.82 | 0.01 | 0.06 | 0.20 | 0.03 | 0.32 | 18.39 | 1.20 | 1.04 | 1.05 | 0.17 | 0.00 |

**Table S9** Flory-Huggins parameter ($\chi_{ij}$) of coarse-grained beads at 333.15 K

| **333.18K** | **$A_2$** | **$A_3$** | **$A_4$** | **$A_6$** | **$R_2$** | **$R_3$** | **$R_4$** | **$O_1$** | **$O_2$** | **S** | **$N_1$** | **$N_2$** | **T** | **W** | **PAM** | **$P_1$** | **$P_2$** | **$P_3$** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **$A_2$** | 0.00 | | | | | | | | | | | | | | | | | |
| **$A_3$** | 0.18 | 0.00 | | | | | | | | | | | | | | | | |
| **$A_4$** | 0.47 | 0.06 | 0.00 | | | | | | | | | | | | | | | |
| **$A_6$** | 0.69 | 0.16 | 0.03 | 0.00 | | | | | | | | | | | | | | |
| **$R_2$** | 0.00 | 0.16 | 0.42 | 0.64 | 0.00 | | | | | | | | | | | | | |
| **$R_3$** | 0.05 | 0.04 | 0.22 | 0.39 | 0.04 | 0.00 | | | | | | | | | | | | |
| **$R_4$** | 0.09 | 0.03 | 0.20 | 0.37 | 0.07 | 0.00 | 0.00 | | | | | | | | | | | |
| **$O_1$** | 1.85 | 0.91 | 0.57 | 0.35 | 1.75 | 1.40 | 1.45 | 0.00 | | | | | | | | | | |
| **$O_2$** | 1.72 | 0.93 | 0.63 | 0.41 | 1.62 | 1.37 | 1.46 | 0.01 | 0.00 | | | | | | | | | |
| **S** | 0.82 | 0.25 | 0.08 | 0.02 | 0.76 | 0.52 | 0.51 | 0.18 | 0.24 | 0.00 | | | | | | | | |
| **$N_1$** | 1.47 | 0.65 | 0.36 | 0.19 | 1.38 | 1.07 | 1.09 | 0.02 | 0.05 | 0.08 | 0.00 | | | | | | | |
| **$N_2$** | 0.57 | 0.13 | 0.02 | 0.00 | 0.52 | 0.32 | 0.31 | 0.31 | 0.35 | 0.02 | 0.17 | 0.00 | | | | | | |
| **T** | 0.15 | 0.01 | 0.14 | 0.29 | 0.12 | 0.02 | 0.01 | 1.33 | 1.37 | 0.43 | 0.98 | 0.25 | 0.00 | | | | | |
| **W** | 16.52 | 16.73 | 18.05 | 16.95 | 15.74 | 18.61 | 22.00 | 13.19 | 9.13 | 13.64 | 13.63 | 13.19 | 23.52 | 0.00 | | | | |
| **PAM** | 4.29 | 3.11 | 2.68 | 2.20 | 4.09 | 3.93 | 4.29 | 0.88 | 0.56 | 1.64 | 1.13 | 1.87 | 4.26 | 6.08 | 0.00 | | | |
| **$P_1$** | 0.07 | 0.49 | 0.95 | 1.26 | 0.08 | 0.26 | 0.34 | 2.72 | 2.46 | 1.38 | 2.25 | 1.03 | 0.47 | 18.29 | 5.44 | 0.00 | | |
| **$P_2$** | 2.31 | 1.27 | 0.88 | 0.60 | 2.18 | 1.84 | 1.92 | 0.04 | 0.01 | 0.37 | 0.11 | 0.53 | 1.81 | 11.67 | 0.56 | 3.25 | 0.00 | |
| **$P_3$** | 0.35 | 0.05 | 0.00 | 0.02 | 0.32 | 0.17 | 0.16 | 0.42 | 0.44 | 0.06 | 0.26 | 0.01 | 0.12 | 11.12 | 1.92 | 0.71 | 0.65 | 0.00 |

**Table S10** Conservative force parameter ($a_{ij}$) of coarse-grained beads at 303.15 K

| **303.15K** | **$A_2$** | **$A_3$** | **$A_4$** | **$A_6$** | **$R_2$** | **$R_3$** | **$R_4$** | **$O_1$** | **$O_2$** | **S** | **$N_1$** | **$N_2$** | **W** | **PAM** | **$P_1$** | **$P_2$** | **$P_3$** | **$P_4$** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **$A_2$** | 78.00 | | | | | | | | | | | | | | | | | |
| **$A_3$** | 78.55 | 78.00 | | | | | | | | | | | | | | | | |
| **$A_4$** | 79.23 | 78.12 | 78.00 | | | | | | | | | | | | | | | |
| **$A_6$** | 79.83 | 78.36 | 78.07 | 78.00 | | | | | | | | | | | | | | |
| **$R_2$** | 78.03 | 78.84 | 79.67 | 80.36 | 78.00 | | | | | | | | | | | | | |
| **$R_3$** | 78.00 | 78.53 | 79.23 | 79.88 | 78.06 | 78.00 | | | | | | | | | | | | |
| **$R_4$** | 78.08 | 78.30 | 78.88 | 79.47 | 78.22 | 78.05 | 78.00 | | | | | | | | | | | |
| **$O_1$** | 83.50 | 80.70 | 79.88 | 79.21 | 84.33 | 83.86 | 83.39 | 78.00 | | | | | | | | | | |
| **$O_2$** | 83.92 | 81.39 | 80.65 | 79.91 | 84.63 | 84.51 | 84.30 | 78.14 | 78.00 | | | | | | | | | |
| **S** | 80.26 | 78.65 | 78.26 | 78.06 | 80.79 | 80.37 | 79.99 | 78.64 | 79.16 | 78.00 | | | | | | | | |
| **$N_1$** | 82.21 | 79.81 | 79.13 | 78.63 | 82.94 | 82.46 | 82.00 | 78.09 | 78.41 | 78.26 | 78.00 | | | | | | | |

| | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **$N_2$** | 79.72 | 78.39 | 78.11 | 78.01 | 80.17 | 79.80 | 79.46 | 78.89 | 79.42 | 78.02 | 78.43 | 78.00 | | | | | | |
| **W** | 133.66 | 134.93 | 140.80 | 137.40 | 133.59 | 145.68 | 156.05 | 124.22 | 108.50 | 125.76 | 125.97 | 123.22 | 78.00 | | | | | |
| **PAM** | 91.76 | 88.15 | 87.29 | 85.82 | 92.74 | 93.33 | 93.67 | 81.14 | 79.57 | 83.83 | 82.10 | 84.20 | 99.16 | 78.00 | | | | |
| **$P_1$** | 78.30 | 78.03 | 78.24 | 78.54 | 78.51 | 78.28 | 78.13 | 81.00 | 81.55 | 78.85 | 80.09 | 78.56 | 127.36 | 87.96 | 78.00 | | | |
| **$P_2$** | 92.35 | 88.06 | 86.91 | 85.38 | 93.52 | 93.62 | 93.59 | 80.62 | 79.23 | 83.47 | 81.60 | 83.96 | 107.42 | 78.07 | 88.14 | 78.00 | | |
| **$P_3$** | 84.81 | 82.30 | 81.60 | 80.75 | 85.50 | 85.62 | 85.59 | 78.46 | 78.08 | 79.79 | 78.87 | 80.06 | 102.23 | 78.83 | 82.35 | 78.57 | 78.00 | |
| **$P_4$** | 84.77 | 81.14 | 80.09 | 79.30 | 85.87 | 85.01 | 84.27 | 78.01 | 78.26 | 78.67 | 78.06 | 78.98 | 145.44 | 82.46 | 81.61 | 81.66 | 78.76 | 78.00 |

**Table S11** Conservative force parameter ($a_{ij}$) of coarse-grained beads at 318.15 K

| **318.15K** | **$A_2$** | **$A_3$** | **$A_4$** | **$A_6$** | **$R_2$** | **$R_3$** | **$R_4$** | **$O_1$** | **$O_2$** | **S** | **$N_1$** | **$N_2$** | **W** | **PAM** | **$P_1$** | **$P_2$** | **$P_3$** | **$P_4$** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **$A_2$** | 78.00 | | | | | | | | | | | | | | | | | |
| **$A_3$** | 78.60 | 78.00 | | | | | | | | | | | | | | | | |
| **$A_4$** | 79.42 | 78.15 | 78.00 | | | | | | | | | | | | | | | |
| **$A_6$** | 80.07 | 78.42 | 78.08 | 78.00 | | | | | | | | | | | | | | |
| **$R_2$** | 78.02 | 78.83 | 79.76 | 80.48 | 78.00 | | | | | | | | | | | | | |
| **$R_3$** | 78.03 | 78.41 | 79.13 | 79.76 | 78.10 | 78.00 | | | | | | | | | | | | |
| **$R_4$** | 78.12 | 78.26 | 78.89 | 79.49 | 78.25 | 78.03 | 78.00 | | | | | | | | | | | |
| **$O_1$** | 84.17 | 81.06 | 80.06 | 79.35 | 84.80 | 83.93 | 83.72 | 78.00 | | | | | | | | | | |
| **$O_2$** | 84.10 | 81.40 | 80.53 | 79.79 | 84.61 | 84.12 | 84.13 | 78.08 | 78.00 | | | | | | | | | |
| **S** | 80.47 | 78.70 | 78.25 | 78.06 | 80.87 | 80.21 | 79.98 | 78.76 | 79.10 | 78.00 | | | | | | | | |
| **$N_1$** | 82.35 | 79.79 | 79.02 | 78.55 | 82.88 | 82.07 | 81.82 | 78.17 | 78.42 | 78.22 | 78.00 | | | | | | | |
| **$N_2$** | 79.78 | 78.38 | 78.08 | 78.00 | 80.12 | 79.56 | 79.34 | 79.12 | 79.45 | 78.04 | 78.44 | 78.00 | | | | | | |
| **W** | 132.64 | 133.34 | 138.42 | 135.05 | 132.10 | 142.82 | 153.42 | 121.56 | 107.41 | 123.94 | 124.49 | 121.98 | 78.00 | | | | | |
| **PAM** | 91.99 | 88.12 | 87.00 | 85.54 | 92.66 | 92.65 | 93.33 | 80.78 | 79.55 | 83.65 | 82.10 | 84.23 | 98.29 | 78.00 | | | | |
| **$P_1$** | 78.38 | 78.01 | 78.24 | 78.55 | 78.55 | 78.24 | 78.13 | 81.21 | 81.42 | 78.83 | 79.96 | 78.49 | 125.60 | 87.70 | 78.00 | | | |
| **$P_2$** | 93.05 | 88.42 | 86.99 | 85.43 | 93.88 | 93.37 | 93.74 | 80.47 | 79.34 | 83.57 | 81.85 | 84.28 | 105.74 | 78.04 | 88.22 | 78.00 | | |
| **$P_3$** | 84.86 | 82.20 | 81.35 | 80.52 | 85.34 | 85.06 | 85.25 | 78.31 | 78.07 | 79.65 | 78.83 | 80.02 | 101.52 | 78.86 | 82.11 | 78.69 | 78.00 | |
| **$P_4$** | 85.33 | 81.37 | 80.13 | 79.32 | 86.16 | 84.81 | 84.36 | 78.02 | 78.21 | 78.70 | 78.10 | 79.13 | 142.36 | 82.19 | 81.66 | 81.67 | 78.61 | 78.00 |

**Table S12** Conservative force parameter ($a_{ij}$) of coarse-grained beads at 333.15 K

| **333.15K** | **$A_2$** | **$A_3$** | **$A_4$** | **$A_6$** | **$R_2$** | **$R_3$** | **$R_4$** | **$O_1$** | **$O_2$** | **S** | **$N_1$** | **$N_2$** | **W** | **PAM** | **$P_1$** | **$P_2$** | **$P_3$** | **$P_4$** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **$A_2$** | 78.00 | | | | | | | | | | | | | | | | | |
| **$A_3$** | 78.64 | 78.00 | | | | | | | | | | | | | | | | |
| **$A_4$** | 79.64 | 78.20 | 78.00 | | | | | | | | | | | | | | | |
| **$A_6$** | 80.42 | 78.55 | 78.09 | 78.00 | | | | | | | | | | | | | | |
| **$R_2$** | 78.00 | 78.56 | 79.48 | 80.23 | 78.00 | | | | | | | | | | | | | |
| **$R_3$** | 78.19 | 78.16 | 78.76 | 79.36 | 78.15 | 78.00 | | | | | | | | | | | | |
| **$R_4$** | 78.30 | 78.11 | 78.69 | 79.30 | 78.24 | 78.01 | 78.00 | | | | | | | | | | | |
| **$O_1$** | 84.49 | 81.20 | 79.98 | 79.21 | 84.12 | 82.92 | 83.07 | 78.00 | | | | | | | | | | |
| **$O_2$** | 84.00 | 81.24 | 80.19 | 79.44 | 83.65 | 82.81 | 83.10 | 78.04 | 78.00 | | | | | | | | | |
| **S** | 80.86 | 78.88 | 78.29 | 78.06 | 80.65 | 79.81 | 79.79 | 78.64 | 78.82 | 78.00 | | | | | | | | |

| | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **$N_1$** | 83.16 | 80.28 | 79.25 | 78.67 | 82.84 | 81.73 | 81.81 | 78.07 | 78.19 | 78.28 | 78.00 | | | | | | | |
| **$N_2$** | 79.98 | 78.45 | 78.07 | 78.00 | 79.82 | 79.12 | 79.09 | 79.08 | 79.24 | 78.06 | 78.60 | 78.00 | | | | | | |
| **W** | 135.80 | 136.55 | 141.19 | 137.34 | 133.10 | 143.12 | 155.01 | 124.18 | 109.94 | 125.74 | 125.70 | 124.15 | 78.00 | | | | | |
| **PAM** | 93.01 | 88.89 | 87.37 | 85.71 | 92.32 | 91.76 | 93.00 | 81.07 | 79.96 | 83.75 | 81.94 | 84.56 | 99.26 | 78.00 | | | | |
| **$P_1$** | 78.23 | 79.72 | 81.31 | 82.40 | 78.27 | 78.90 | 79.20 | 87.52 | 86.60 | 82.84 | 85.86 | 81.62 | 142.01 | 97.04 | 78.00 | | | |
| **$P_2$** | 86.07 | 82.46 | 81.08 | 80.10 | 85.65 | 84.44 | 84.73 | 78.13 | 78.02 | 79.29 | 78.39 | 79.86 | 118.85 | 79.95 | 89.37 | 78.00 | | |
| **$P_3$** | 79.24 | 78.17 | 78.00 | 78.06 | 79.12 | 78.61 | 78.58 | 79.46 | 79.52 | 78.20 | 78.91 | 78.04 | 116.93 | 84.71 | 80.47 | 80.27 | 78.00 | |
| **$P_4$** | 80.47 | 78.40 | 78.02 | 78.05 | 80.27 | 79.22 | 79.10 | 80.09 | 80.45 | 78.24 | 79.27 | 78.03 | 165.02 | 89.29 | 82.79 | 81.38 | 78.01 | 78.00 |

**Table S13** Construction details of CHPAMAM-oil-water simulation systems

| Temperature | Number | Water | Hexadecane | Asphaltene | Resin | HPAM | CHPAMAM |
|---|---|---|---|---|---|---|---|
| **303.15 K** | 1 | 88.0 % | 8.6 % | 0.4 % | 1.0 % | 2.0 % | 80ppm |
| | 2 | 78.0 % | 17.2 % | 0.8 % | 2.0 % | 2.0 % | |
| | 3 | 68.0 % | 25.8 % | 1.2 % | 3.0 % | 2.0 % | |
| | 4 | 58.0 % | 34.4 % | 1.6 % | 4.0 % | 2.0 % | |
| **318.15 K** | 5 | 88.0 % | 8.6 % | 0.4 % | 1.0 % | 2.0 % | |
| | 6 | 78.0 % | 17.2 % | 0.8 % | 2.0 % | 2.0 % | |
| | 7 | 68.0 % | 25.8 % | 1.2 % | 3.0 % | 2.0 % | |
| | 8 | 58.0 % | 34.4 % | 1.6 % | 4.0 % | 2.0 % | |
| **333.15 K** | 9 | 88.0 % | 8.6 % | 0.4 % | 1.0 % | 2.0 % | |
| | 10 | 78.0 % | 17.2 % | 0.8 % | 2.0 % | 2.0 % | |
| | 11 | 68.0 % | 25.8 % | 1.2 % | 3.0 % | 2.0 % | |
| | 12 | 58.0 % | 34.4 % | 1.6 % | 4.0 % | 2.0 % | |

## IX. Characteristic properties of CHPAMAM demulsifiers

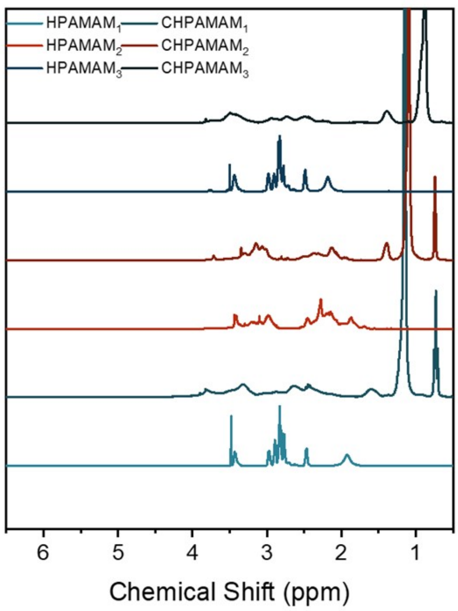

**Fig. S2** $^1$H NMR spectra of HPAMAM and CHPAMAM samples.

**Table S14** Characterization of synthesized HPAMAM and CHPAMAM samples.

| Polymer | $RNH_2$ | $R_2NH$ | $R_3N$ | HLB | Size (nm) |
|---|---|---|---|---|---|
| HPAMAM$_1$ | 27 | 50 | 24 | 13.15 | 3.97 |
| HPAMAM$_2$ | 52 | 121 | 36 | 14.26 | 4.46 |
| HPAMAM$_3$ | 106 | 218 | 94 | 14.51 | 5.06 |
| CHPAMAM$_{1\text{-}15\%}$ | 17 | 44 | 24 | 8.13 | 4.12 |
| CHPAMAM$_{2\text{-}5\%}$ | 44 | 118 | 36 | 12.14 | 4.86 |
| CHPAMAM$_{2\text{-}10\%}$ | 34 | 117 | 36 | 10.49 | 5.11 |
| CHPAMAM$_{2\text{-}15\%}$ | 31 | 111 | 36 | 9.91 | 5.37 |
| CHPAMAM$_{2\text{-}20\%}$ | 22 | 108 | 36 | 8.31 | 5.78 |
| CHPAMAM$_{3\text{-}15\%}$ | 65 | 196 | 94 | 9.06 | 6.01 |

## X. The evaluation experiment of HPAMAM demulsification effect

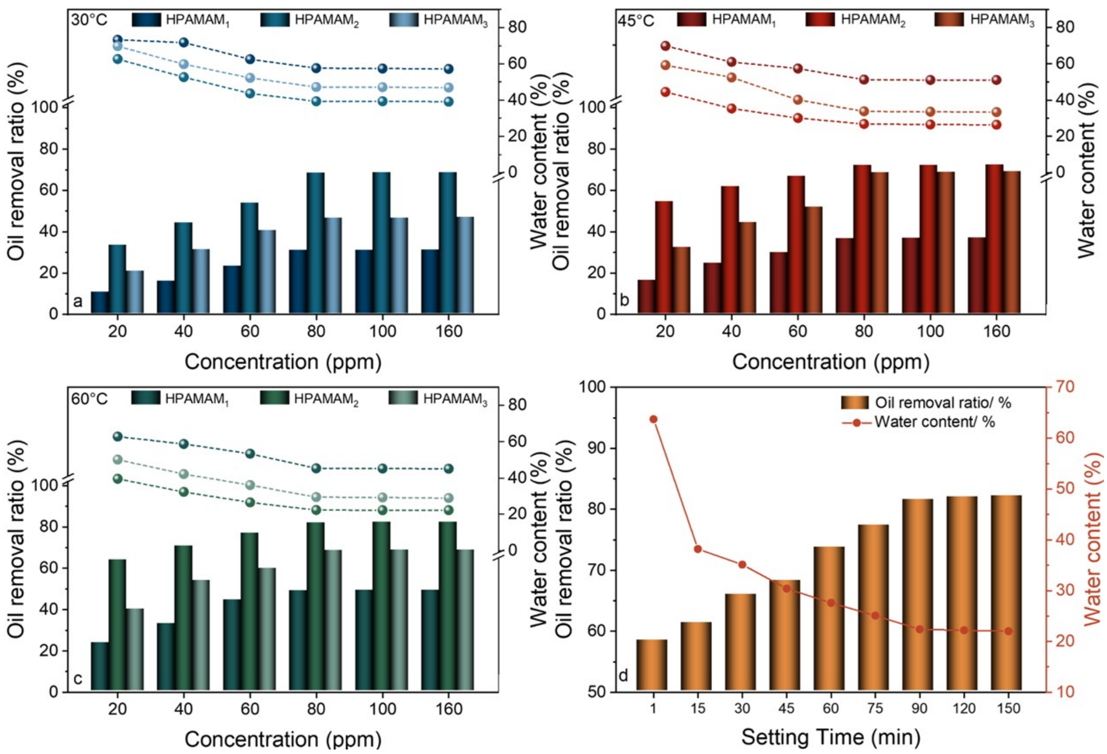


**Fig. S3** Effects of demulsifier concentration and operation temperature on the demulsification performance (column: oil removal ratio of emulsions and line+symbol: water content of oil phase) with CHPAMAM as demulsifiers after 40 min at different temperatures ranging from 30 ºC to 60 ºC for the emulsions with oil-water ratios of 1:9.

## XI. The demulsification performance of CHPAMAM in different emulsions

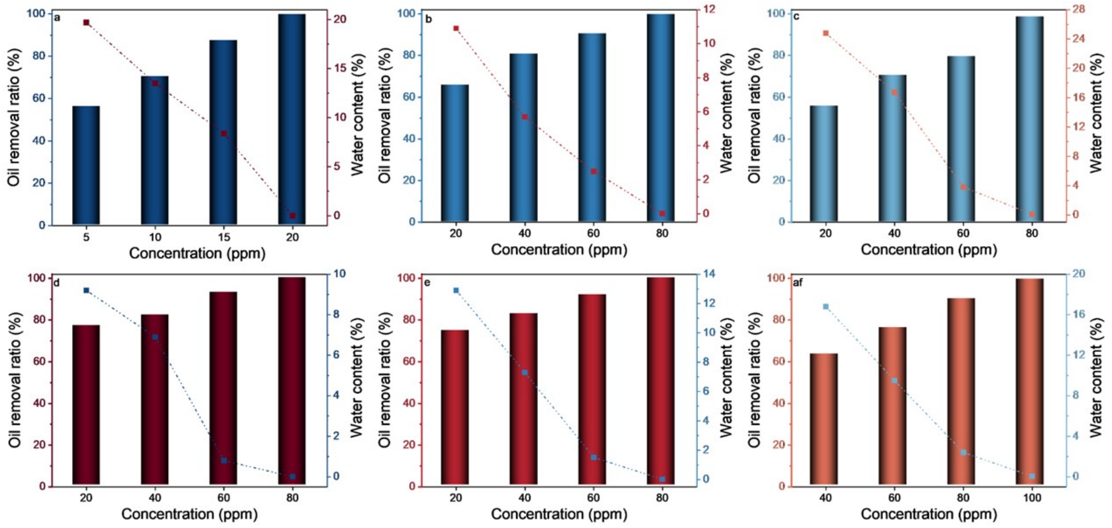


**Fig. S4** Demulsification performance of CHPAMAM demulsifier on (a) crude oil/ water emulsions with 50 % crude oil after setting for 30 min, (b) water/ crude oil emulsions with 10 % water after setting for 40 min, (c) water/ bitumen emulsions with 5.0 % water after setting for 30 min, (d) light crude oil/ water emulsions with 40 % light crude oil after setting for 30 min, (e) crude oil/ water emulsions with 1.0 % crude oil after setting for 10 min, (f) water/ crude oil emulsions with 50 % crude oil after setting for 20 min.

## XII. The tendency of the viscous modulus with CHPAMAM at various oscillation frequencies

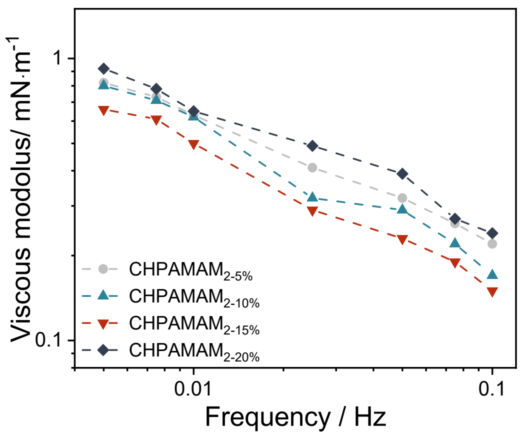


**Fig. S5** Effect of the oscillating frequency on viscous modulus of oil-water interface containing Span 80 and Tween 80 with 80 ppm CHPAMAM demulsifiers.

## XIII. Simulation of dissipative particle dynamics

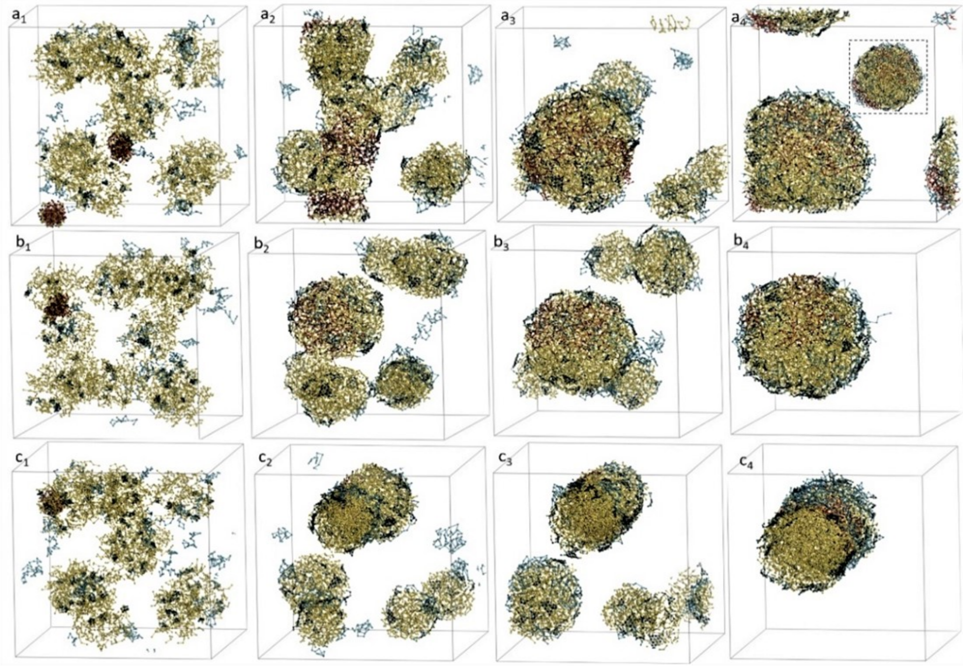


**Fig.S6** Effect of temperature on the demulsificaton process for the emulsions of oil-water ratios 2:8 with CHPAMAM during the DPD simulation (Model basic parameters: temperature is (a) 303.15K, (b) 318.15K, or (c) 333.15K, and CHPAMAM concentration is 80 ppm) at different time steps: ($a_1$-$c_1$) 5 $\times 10^4$steps; ($a_2$-$c_2$) 20 $\times 10^4$steps; ($a_3$-$c_3$) 160 $\times 10^4$steps; ($a_4$-$c_4$) 240 $\times 10^4$steps.

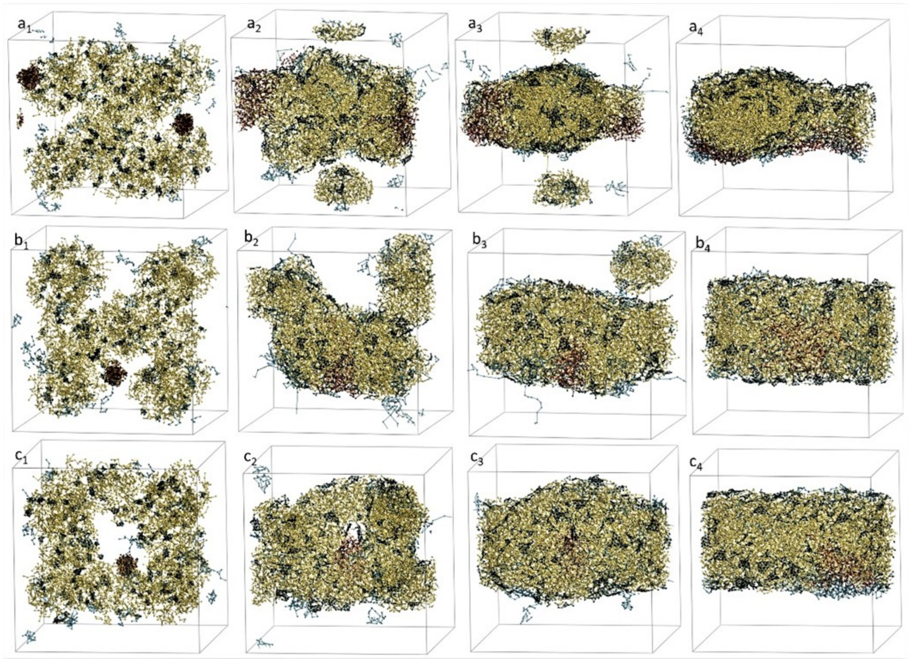


**Fig.S7** Effect of temperature on the demulsificaton process for the emulsions of oil-water ratios 3:7 with CHPAMAM during the DPD simulation (Model basic parameters: Temperature is (a) 303.15K, (b) 318.15K, (c) 333.15K, respectively, and CHPAMAM concentration is 80 ppm) at different time steps: ($a_1$-$c_1$) 5 $\times 10^4$steps; ($a_2$-$c_2$) 20 $\times 10^4$steps; ($a_3$-$c_3$) 160 $\times 10^4$steps; ($a_4$-$c_4$) 240 $\times 10^4$steps.

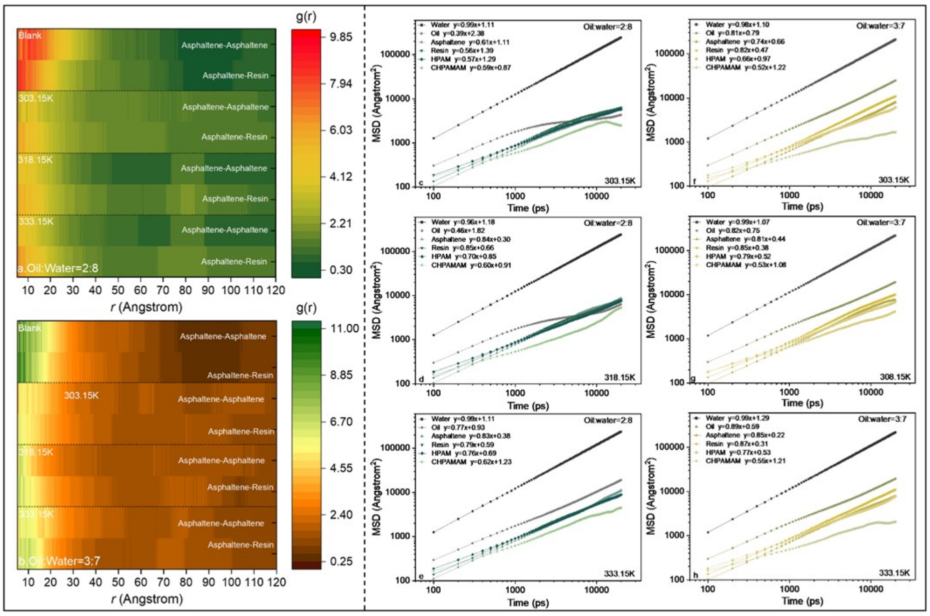


**Fig.S8** Radial distribution functions of asphaltene and asphaltene, asphaltene and resin in emulsions with oil-water ratios (a) 2:8 and (b) 3:7 after adding 80 ppm CHPAMAM at different temperatures. Mean square displacements of each component in emulsions with oil-water ratios (c-e) 1:9 and (f-h) 4:6 after adding 80 ppm CHPAMAM at different temperatures.

# XIV. Components of crude oil produced emulsions

**Table S15** Characteristics of produced emulsions from two China oilfields

| Parameter | value | Parameter | value |
|---|---|---|---|
| Xinan Oilfield | | | |
| Oil content | 13.4 % | Salinity | 4315.5 mg $L^{-1}$ |
| pH | 8.8 | $Mg^{2+}$ | 10.3 mg $L^{-1}$ |
| Density at 293 K | 0.90 g $cm^{-3}$ | $Ca^{2+}$ | 34.5 mg $L^{-1}$ |
| Viscocity at 329 K | 89.2 mPa s | $K^{+}+Na^{+}$ | 2493.1 mg $L^{-1}$ |
| Asphaltene | 2.7 % | $Cl^{-}$ | 2034.2 mg $L^{-1}$ |
| Resin | 19.4 % | $HCO_3^{-}$ | 1469.4 mg $L^{-1}$ |
| Xinjiang Oilfield | | | |
| Oil content | 38.7 % | Salinity | 10451.8 mg $L^{-1}$ |
| pH | 10.7 | $Mg^{2+}$ | 15.3 mg $L^{-1}$ |
| Density at 293 K | 0.98 g $cm^{-3}$ | $Ca^{2+}$ | 29.7 mg $L^{-1}$ |
| Viscocity at 329 K | 6250.3 mPa s | $K^{+}+Na^{+}$ | 5128.7 mg $L^{-1}$ |
| Asphaltene | 10.6 % | $Cl^{-}$ | 4962.6 mg $L^{-1}$ |
| Resin | 24.3 % | $HCO_3^{-}$ | 1531.2 mg $L^{-1}$ |