Electronic Supplementary Information

A pH-sensitive W/O Emulsion for the Preparation and Rapid Dissolution of Polyacrylamide-based Friction Reducer

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Fig. S1 ^{1}H NMR spectra of DM-OA in DMSO-d$_6$.

Fig. S2 Digital images of monomer emulsion stabilized by 3 wt% DM-OA at 50 °C (a) after 0 h (b) after 12 h.

Fig. S3 Picture of DM-OA aqueous solution at different pH.

Fig. S4 Molecular morphology distribution. (a)HOA (b)DMCHA

Fig. S5 Interfacial tension between monomer aqueous solution and liquid paraffin at different pH values.

Fig. S6 The effect of oil-water ratio on the stability of monomer emulsion.

Fig. S7 The influence of the amount of emulsifier on the stability of monomer emulsion.

Fig. S8 Digital images of monomer emulsion stabilized by 3 wt% DM-OA at 50 °C

Fig. S9 The inverse polymer emulsion stabilized by 3 wt% DM-OA.

S1 Determination of intrinsic viscosity and molecular weight.
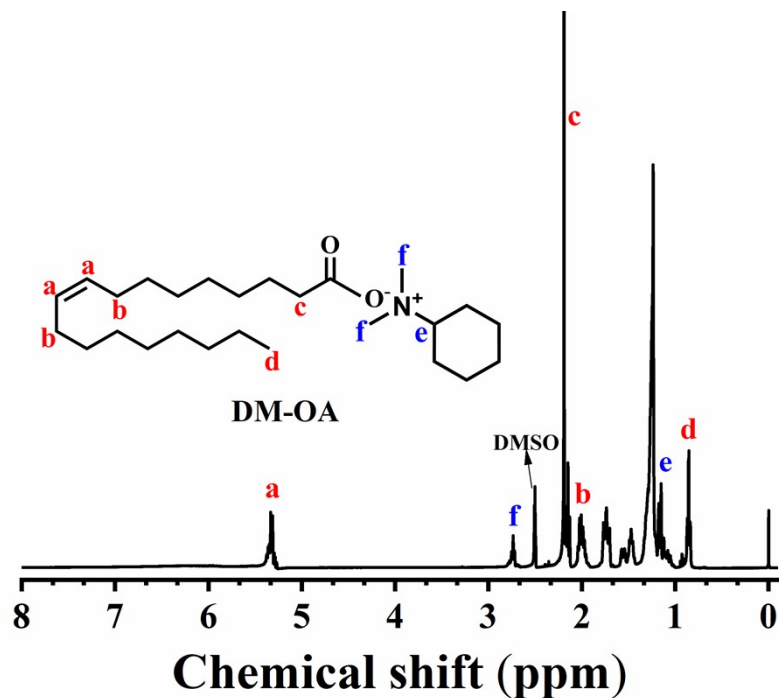
1 Characterization of DM-OA complex

Fig. S1 ^{1}H NMR spectra of DM-OA in DMSO-d_6.

The structural information of DM-OA can be obtained by ^{1}H NMR analysis (Fig. S1). The proton signals of $\delta = 5.33$ ppm and $\delta = 2.73$ ppm correspond to the protons in the alkene (a) and methylene (f) of DM-OA; Methyl (d), methylene (b, c) and methylene (e) protons were found at $\delta = 0.86, 2.19, 2.02$ and 1.15 ppm, respectively; The proton signals of other alkyl chains all appear in the high field region, and the integral value of each proton signal is in good agreement with the theoretical value. ^{1}H NMR analysis showed that DM-OA had been successfully synthesized.
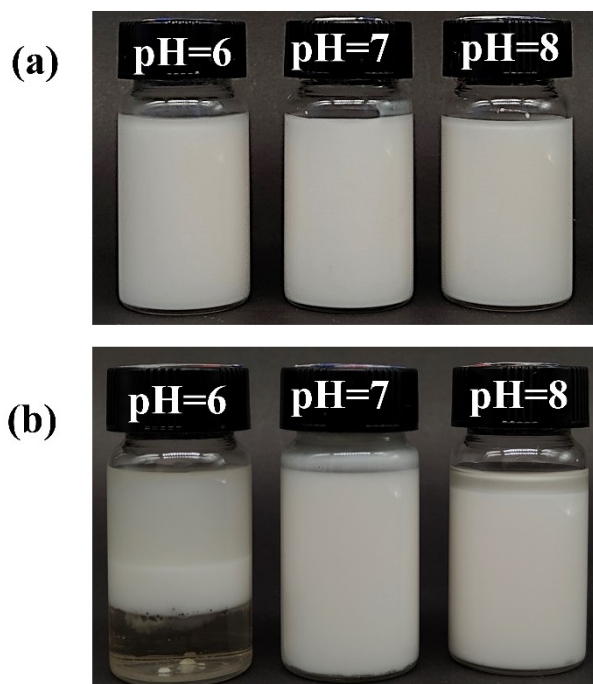
2. Digital images of monomer emulsion

Fig. S2 Digital images of monomer emulsion stabilized by 2 wt % DM-OA at 50 °C (a) after 0 h (b) after 12 h

3. The pH responsiveness of DM-OA.

To demonstrate the responsiveness of emulsions, we investigated the pH responsiveness of DM-OA. The pH of the solution was changed by adding HCl/NaOH to a 1wt% DM-OA aqueous solution. The initial pH of the DM-OA solution is 8.88. Later, when HCl was added to adjust the pH to 5.06, insoluble substances appeared in the solution. Finally, when the pH was increased to 9.00, the insoluble matter disappeared completely (Fig. S3). These results show that the D-OA complex has good pH response characteristics.
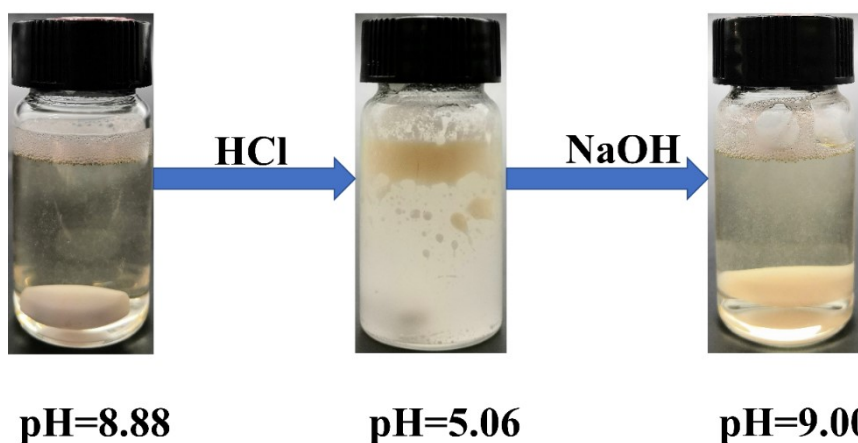
pH=8.88   pH=5.06   pH=9.00

Fig. S3 Picture of DM-OA aqueous solution at different pH

The pKa of DMCHA and HOA are 10.72 and 4.99, respectively (obtained from www. chemicalbook.com), based on which the distribution curve is drawn (Fig. S4). When the pH is 8.88, the aqueous solution mainly consists of most DMCHA$^+$ and OA$^-$, which has good water solubility. When the pH was reduced to 5.06, the structure of DM-OA was destroyed, DMCHA existed in the form of protic DMCHA$^+$, and HOA existed in the form of 49.2% OA$^-$, so there were insoluble substances. When the pH is raised to 9.00, 60% DMCHA$^+$ and sodium oleate exist in the aqueous solution, almost completely dissolved in the water.
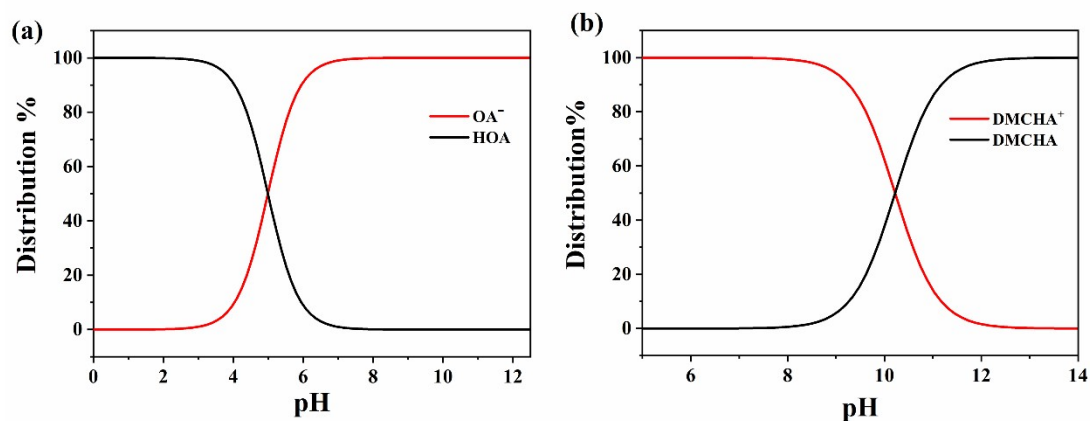

Fig. S4 Molecular morphology distribution. (a)HOA (b)DMCHA

As shown from Fig. S5, the interfacial tension between monomer aqueous solution and liquid paraffin decreases to varying degrees with the increase of pH. From low to high pH values, the interfacial tension remains almost constant from pH 3 to 5.86, drops significantly in the pH range of 5.96-8.89, and finally stabilizes at interfacial tension values close to 0 at pH >9. In a nutshell, at low pH, the structure of DM-OA is broken down into $DMCHA^+$ and HOA, and the interfacial tension between oil and water increases, and emulsion demulsification. When the pH is in the range of 6-8, some parts of DM-OA toward to DMCHA and HOA, that DM-OA is a W/O emulsifier. With the gradual increase of pH, DM-OA will be transformed into DMCHA and HOA^-, and then the emulsifier will become an O/W emulsifier, and the emulsion will be transformed into O/W emulsion.
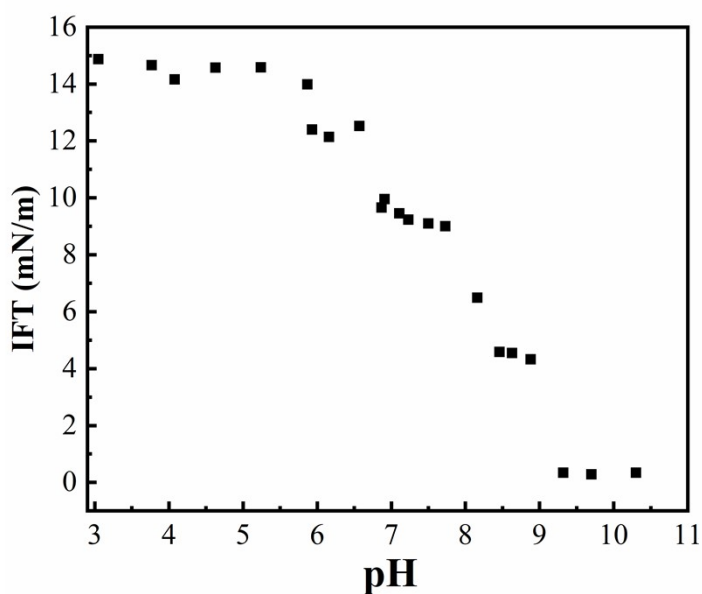

Fig. S5 Interfacial tension between monomer aqueous solution and liquid paraffin at different pH values

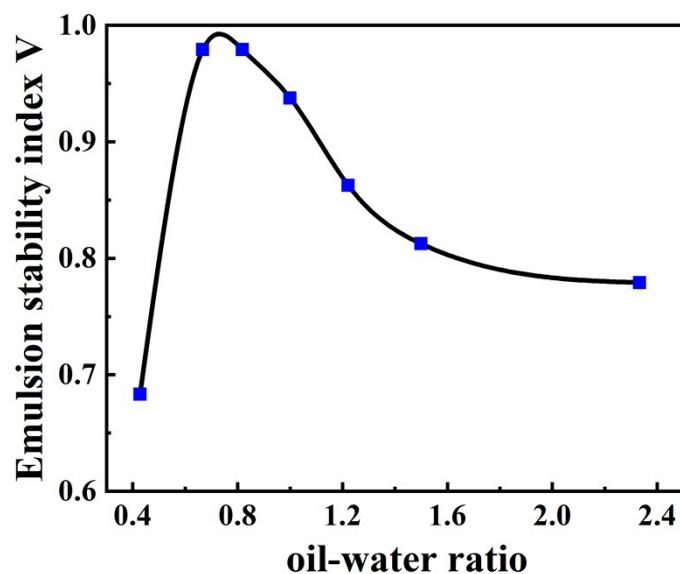**4. Effect of oil-water ratio on the stability of monomer emulsion.**

Fig. S6 The effect of oil-water ratio on the stability of monomer emulsion

5. The influence of the amount of emulsifier on the stability of monomer emulsion.
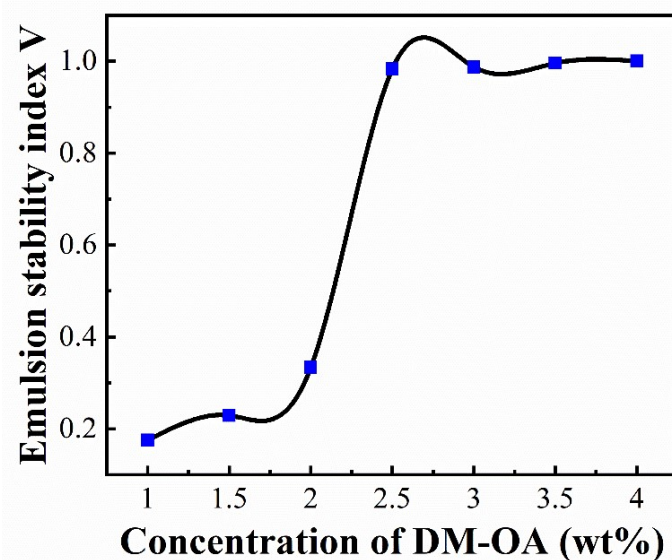

Fig. S7 The influence of the amount of emulsifier on the stability of monomer emulsion

6. Digital images of monomer emulsion stabilized by 3 wt % DM-OA

at 50 ℃

Fig. S8 Digital images of monomer emulsion stabilized by 3 wt % DM-

OA at 50℃

7. The Polyacrylamide inverse polymer emulsion stabilized by 3 wt %

DM-OA.

Fig. S9 The Polyacrylamide emulsion stabilized by 3 wt % DM-OA

8. Determination of intrinsic viscosity and molecular weight

The measurements and calculation methods for the intrinsic viscosity

were realized following the method described by S. Krishnamoorthi et al[1].

The intrinsic viscosity was employed to calculate viscosity–average

molecular weights (M_W), using the Mark–Houwink equation (1),

$$[\eta] = K \times M_W^a$$
(1)

In this case, the constants a and K were 0.80 and 6.31×10^{-5}, respectively.

Viscosity of each solution was measured three times by Ubbelohde viscometer. The intrinsic viscosity, [η]=1017 mL/g, was determined from intercept value of a linear regression of relationship between the specific viscosity and polymer concentration. The calculation revealed that the viscosity-average molecular weight of P(AM-AA-AMPS) is 3.24×10^{6} g/mol.

References

1.   E. Sonker, R. Tiwari, P. Adhikary, K. Kumar and S. Krishnamoorthi, *Polymer Engineering & Science*, 2019, **59**, 1175-1181.