Supporting Information

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SI Text

Electrophoretic Mobility Measurements of the Microgel Emulsions. To study the charge properties of the droplets stabilized by the oppositely charged MAA and AEM microgels, we perform the electrophoretic mobility measurements on the MAA-, AEM-emulsion and their mixture at different conditions.

The mobility measurements are carried out first with the individual emulsions with either the MAA microgels or the AEM microgels at a certain pH. The same sample is then mixed of a dispersion of the oppositely charged microgels with the same volume at the same pH. Laser Doppler Microelectrophoresis technique is employed—the signal comes from forward scattered light of the sample. Therefore, although the emulsion samples prepared at high microgel concentration contain droplets and excess microgels, the signal of the droplets (100–200 μm) dominates over that of the microgels (300–800 nm). The mobility measurement of each sample is started immediately after preparation—the value is obtained within 3 min.

At pH 7, the sign of charges of the two individual emulsions agrees with the sign of charges of the corresponding microgels. Charge reversal is clearly observed for both emulsions after adding the other type of microgels, changing from -1.12 to $+0.66$ μmcm/Vs for MAA-stabilized emulsion and from $+0.76$ to -1.42 μmcm/Vs for the AEM-stabilized emulsion. At pH 3, the mobility of the MAA-stabilized emulsion changes from -0.10 to $+0.43$ μmcm/Vs and that of the AEM-stabilized emulsion from $+0.32$ to $+0.29$ μmcm/Vs. At pH 9, the mobility of the MAA-stabilized emulsion changes from -0.83 to -0.68 μmcm/Vs and the AEM-stabilized emulsion from -0.28 to -0.32 μmcm/Vs, after adding the other type of microgels (Table S1) (1). According to these results, there might be like-charged repulsion at these two conditions. It is understandable that the change is more moderate at pH 3 or 9 than at pH 7, because at pH 3 or 9 one of the two types of microgels does not carry charges. In summary, attraction is present at pH 7 when mixed emulsions do not coalesce; while no attraction (or slight repulsion) is present at pH 3 or 9 when mixed emulsions do coalesce. Electrostatic effects cannot explain the stabilization of such emulsions.

Note that creaming occurs to the emulsions investigated in this work. It is necessary to consider the influence of creaming on the electrophoretic mobility measurement before the above mentioned conclusion can be drawn. For this purpose, we perform the time dependent electrophoretic mobility of an emulsion sample. The electrophoretic mobility of the emulsions is changing over time due to creaming of the droplets (Fig. S1*A*). However, the effect of creaming on the mobility value starts only after 20 min. As the electrophoretic mobility values used in Table S1 are taken within the first few minutes after sample preparation, it is unlikely that they are influenced by creaming.

To further check this assumption, we perform another set of measurements on MAA and AEM emulsions with a solvent mixture of heptane and dichloromethane (12:5, w:w), which has a density of 1 g/cm^3. Because of the density match of solvent mixture and water (both 1 g/cm^3), no creaming occurs in these emulsions. The electrophoretic mobility values of these emulsions (Table S1) (2) are consistent with those of the heptane emulsions. With the confirmation from these two creaming tests, we conclude that indeed the electrophoretic mobility values of the emulsions is reliable, and thus indeed the electrostatic effects cannot explain the noncoalescence/coalescence of the emulsions in this study.

Photobleaching of a Mixed Emulsion Droplet. To study the dynamics of the microgels that are adsorbed at oil–water interface, a photobleaching experiment is carried out. A mixed emulsion is prepared in the microfluidic device at pH 7. Subsequently, an area on the surface of one droplet is selectively bleached by high intensity laser irradiation and thus loses its fluorescence. Fig. S1*B* shows that the bleached area remains without fluorescence at least 10 min after bleaching. See also Movie S4 for the recording of the confocal images during this 10-min time. This experiment demonstrates that on this time scale the microgels do not diffuse within the layer and that there is no exchange with microgels between the interface and the bulk phase; i.e., the interfacial microgels do not desorb.

Heteroaggregation of Microgels at the Oil–Water Interface. When MAA- and AEM- emulsion are prepared at a high microgel concentration, both microgels exist in excess. When the emulsions are mixed, the excess MAA and AEM microgels will likely interact with the droplets and influence their interaction and stability. To demonstrate the interaction of the excess microgels and the droplets, we employ the confocal microscopy to visualize the adsorption of microgels on the emulsion droplets. The emulsion is prepared in a microfluidic device, with the MAA and AEM microgels each at a concentration of 0.5 wt. %.

Two droplet species are observed: red-fluorescent droplets and nonfluorescent droplets (Fig. S1*C*). It is evident that both types of droplets are wrapped in fluorescent outer layers. As described in the main manusript, the AEM microgels are rhodamine-labeled and cover the droplets that consist of Sudan-Blue-dyed heptane. Hence, these droplets show fluorescence in both their core and on their surface—the rhodamine label stains their surface; whereas the Sudan Blue dye labels their core. The logical implication is that the remaining, nonfluorescent structures in this image should be the droplets covered by the MAA microgels. As the MAA microgels are not fluorescently labeled, one would expect these droplets to be invisible in the image. Nevertheless, we see them covered with a fluorescent layer, too. The most plausible explanation for this finding is that there are also fluorescently labeled AEM microgels on these droplets.

The red-tagged AEM microgels that also appear on the originally nonfluorescent, MAA-covered droplets are most probably from the continuous phase. Three facts argue for this assumption: first, it is visible in the confocal image that there are fluorescent microgels in the continuous phase, even though the microgel concentration is only 0.5 wt. % prior to the emulsification. Second, when performing a simple test by mixing individually prepared, MAA-covered droplets with plain AEM microgels, we see that the resultant droplets are stable and fluorescence is observed on the originally uncolored droplet surface (Fig. S1*D*); this observation proves that free AEM microgels are driven to the oppositely charged droplet surface. Third, the possibility of one microgel species migrating from an emulsion droplet to a droplet of another type is ruled out by the photobleaching experiment (Fig. S1*B*). In conclusion, when existing in excess, the AEM microgels adsorb to the droplets that are oppositely charged—the MAA droplets. Although not visualized in this experiment, it is reasonable to expect the MAA microgels in excess also adsorb to the AEM droplets. As a result, when mixing the MAA and the AEM emulsions with excess microgels, two new types of droplets with modified surfaces might be generated.

Rheo-Optical Experiements with the Mixed Emulsions. The microfluidic mixing experiments reveal the pH-sensitivity of MAA-AEM mixed emulsions. To explore the behavior of the pH-dependent stability of these emulsions in bulk, we perform the rheo-optical measurements. The results of these measurements are shown in Fig. 4 and discussed in the main text. Here we describe these measurements in detail.

(1) Large amplitude oscillatory shear deformation of the mixed emulsion. For the shear experiment, we apply gradually increasing shear force on the emulsion at different pH (pH 3, pH 7, and pH 10) and observe the sheared emulsion under an optical microscope. For the sample at each pH, a series of oscillation (termed "large amplitude oscillatory shear deformation") is applied at different strain and frequency. Starting from strain = 400 and frequency = 1 Hz, the frequency is increased in 1 Hz steps to up to 9 Hz. Subsequently, maintaining frequency at 9 Hz, the strain is increased to 800 and finally 1,200. Each oscillation step lasts for one minute, after which a micrograph of the sheared sample is taken. The series is stopped when phase separation occurs. The stability of the emulsion is indicated by the strain and frequency at which the sample undergoes phase separation.

(2) Coalescence in the MAA and AEM mixed emulsion at pH 10. In the main text, we discuss that the stability of the mixed emulsion differs at pH 3 and at pH 10, in that at pH 3, all droplets—both the MAA- and AEM- droplets coalesce; whilst at pH 10, macroscopic phase separation appears to involve mainly the AEM droplets (blue) and many MAA-emulsion droplets (yellow) remain stable after shear (Fig. 4 *D* and *F*). However, it is noteworthy that coalescence between MAA- and AEM- droplets also occurred in this sample (Fig. S1*E*). Therefore, the characteristics of the MAA-AEM mixed emulsion at pH 10 and at pH 3 do not differ qualitatively.

Microfluidic Mixing of Emulsions with Reduced Microgel Concentration. As mentioned above, when existing in excess, the MAA and the AEM microgels could modify the droplet surfaces in the mixed emulsion. To reduce this influence in the microfluidic mixing experiment, we use a microfluidic device that allows the excess microgels to be washed away before the droplets are mixed. This is achieved by adding a fivefold excess of plain aqueous phase immediately after forming the droplets, thereby reducing the concentration of microgels in the continuous phase from 0.5 to 0.1 wt. %. We realize this by adding the diluting plain water at a volume flow rate that is five times higher than that of the microgel-laden aqueous stream used to form the droplets; as a result, the droplets are spaced out by a factor of five and the microgels in the continuous phase start to occupy the newly added volume. To enhance this process, the diluted emulsion is flown through a channel with a wiggly shape, introducing turbulences and enhancing the mixing of the old and the newly added, plain aqueous phases. Subsequently, the dilute emulsion enters another cross-junction, where most of the diluted continuous phase is removed by sucking at a negative volume flow rate that is matched to the one used to add the diluting water, restoring the original droplet volume fraction in the continuous phase (Fig. S1*F*). Even at this condition, we observe that the oppositely charged droplets do not coalesce (Movie S5). Although to a much less extent, all droplets are still covered with fluorescent microgels (Fig. S1*G*), the same as observed in the sample prepared at higher microgel concentration (Fig. S1*B*). This observation demonstrates that the noncoalescence behavior observed in the original microfluidic mixing experiment holds true with much less amount of excess microgels.

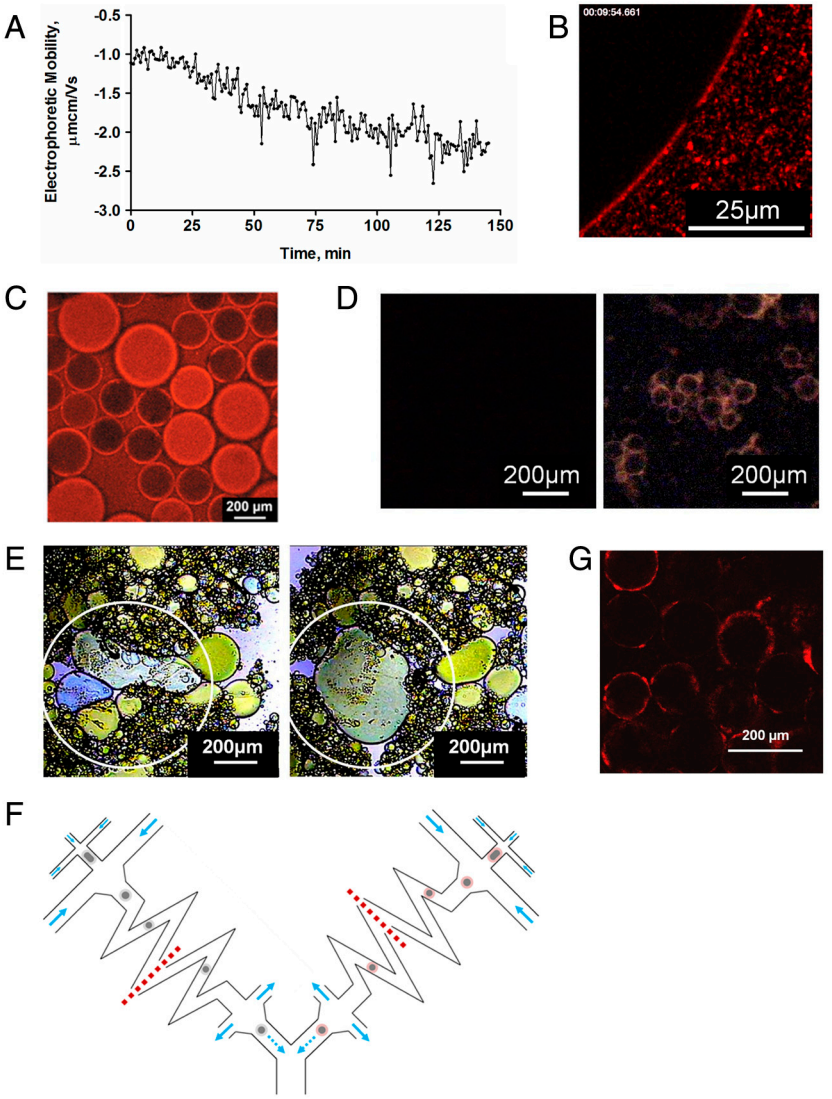
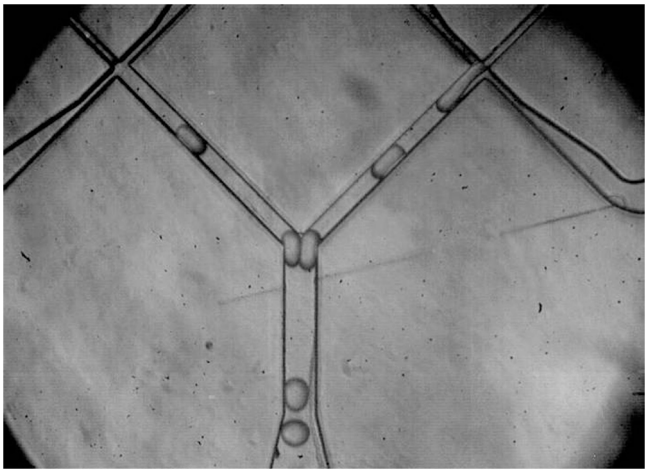
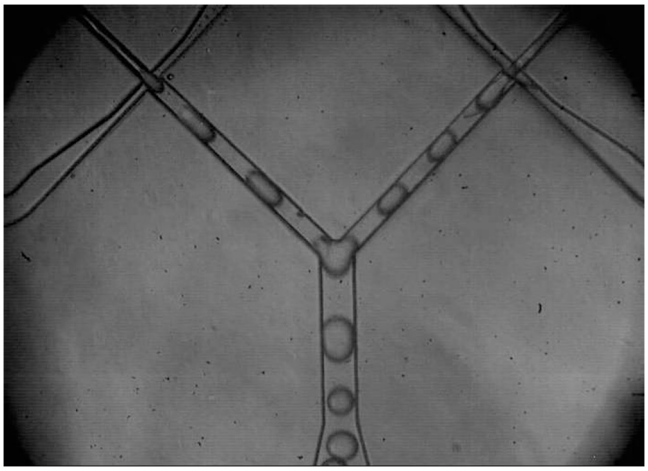


Fig. S1. (*A*) Evolution of the electrophoretic mobility of a MAA-stabilized heptane-in-water emulsion over time. (*B*) Confocal micrograph of a mixed emulsion with oppositely charged, microgel-stabilized heptane droplets in water 10 minutes after photobleaching. (*C*) Confocal micrograph of a mixed emulsion of oppositely charged, microgel-stabilized heptane droplets in water. Dark circles: droplets stabilized by the negatively charged MAA microgels; bright circles: droplets stabilized by the positively charged AEM microgels. (*D*) Fluorescence micrographs of MAA-covered droplets before (*Left*) and after (*Right*) adding AEM-microgels. (*E*) Coalescence in the MAA and AEM mixed emulsion at pH 10 before (*Left*) and after shear forces are applied (*Right*). Shear force of strain = 400 and frequency = 1 Hz is applied for 1 min. The bright yellow color droplets are MAA emulsion droplets dyed with Sudan yellow; the bright blue droplets are AEM emulsion droplets dyed with Sudan blue. (*F*) Microfluidic device used to study the interaction of microgel-stabilized emulsion droplets after a washing step to dilute the concentration of free microgels in the continuous phase. Two drop-forming cross-junctions, two dilution cross-junctions, and two suction cross-junctions are used to generate and wash the different types of emulsions. The first cross-junction on the left side is used to form heptane-in-water droplets stabilized by nonlabeled, negatively charged MAA microgels. The droplets then flow through the left dilution cross-junction (second junction on the left) where plain water is injected at a flow rate that is five times higher than the droplets. The following zic-zac channel allows thorough dilution of the aqueous phase. At the suction cross-junction (third junction on the left), the diluted aqueous phase is removed at a flow rate that matches the injection rate at the dilution cross-junction. The cross-junctions on the right side are used to form and wash heptanes-in-water droplets stabilized by rhodamine-labeled, positively charged AEM microgels. Finally, the washed droplets from the channels on the left side and on the right side meet at the mixing junctions, which serve to study their interaction upon contact. (*G*) Confocal micrograph of a mixed emulsion of oppositely charged, microgel-stabilized heptane droplets in water, prepared from a microfluidic device equipped with washing channels; see *F*. The microgel concentration in the continuous phase is reduced fivefold by the washing steps.



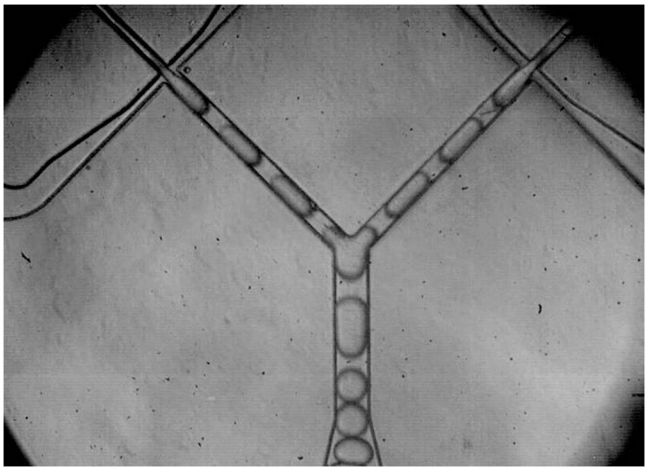
Movie S1. Mixing of droplets stabilized with MAA microgels (left) and AEM microgels (right) in a microfluidic device at pH 7

Movie S1 (MOV)



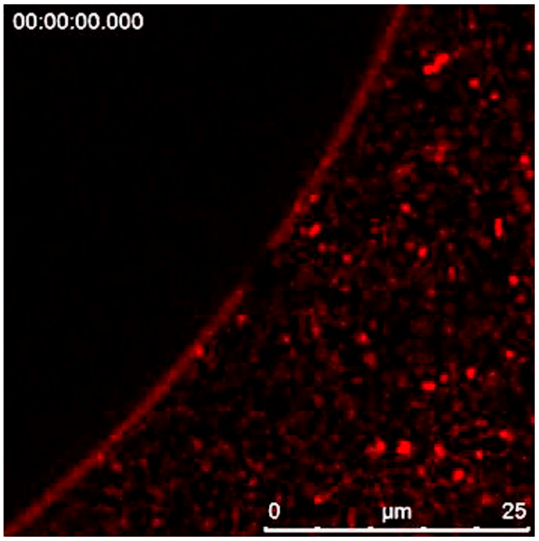
Movie S2. Mixing of droplets stabilized with MAA microgels (left) and AEM microgels (right) in a microfluidic device at pH 4.

Movie S2 (MOV)



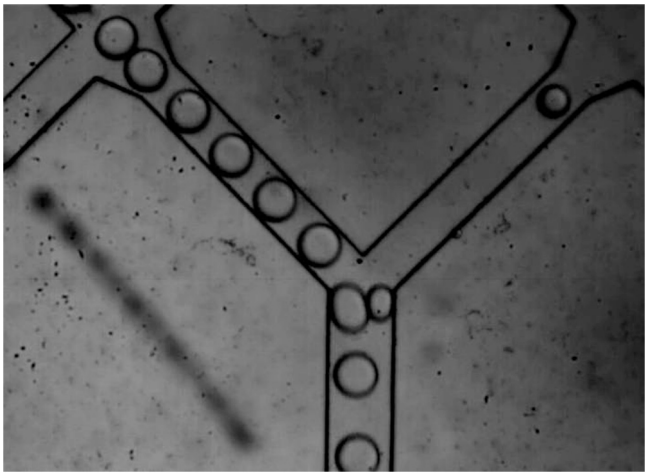
Movie S3. Mixing of droplets stabilized with MAA microgels (left) and AEM microgels (right) in a microfluidic device at pH 9.

Movie S3 (MOV)



Movie S4. Continuous recording of confocal micrographs of a mixed emulsion with oppositely charged, microgel-stabilized heptane droplets in water after photobleaching. A mixed emulsion is prepared in the microfluidic device at pH 7. Subsequently, an area on the surface of one droplet is selectively bleached by high intensity laser irradiation and thus loses the fluorescence. The bleached area is observed for 10 min. The recording of the confocal images during this time shows no change of the bleached area during the whole period

Movie S4 (MOV)



Movie S5. Mixing of droplets stabilized with MAA microgels (left) and AEM microgels (right) in a microfluidic device at pH 7. The continuous phase is diluted from a microgel concentration of 0.5 wt. % to about 0.1 wt.%

Movie S5 (MOV)

Table S1. Electrophoretic mobility of emulsion droplets before and after addition of oppositely charged microgels (heptane-water emulsions)

Mixture		Electrophoretic mobility before mixing $\mu_e 1$, μmcm/Vs	Electrophoretic mobility after mixing $\mu_e 2$, μmcm/Vs
MAA emulsion+AEM microgel	pH 3	−0.10 ± 0.05	+0.43 ± 0.19
	pH 7	−1.12 ± 0.02	+0.66 ± 0.04
	pH 9	−0.83 ± 0.01	−0.68 ± 0.30
AEM emulsion + MAA microgel	pH 3	+0.32 ± 0.06	+0.29 ± 0.18
	pH 7	+0.76 ± 0.10	−1.42 ± 0.21
	pH 9	−0.28 ± 0.19	−0.32 ± 0.06

Heptane dichloromethane mixture at 12:5, w/w.

Table S2. Electrophoretic mobility of emulsion droplets before and after addition of oppositely charged microgels (solvent mixture-water emulsions)

Mixture		Electrophoretic mobility before mixing $\mu_e 1$, μmcm/Vs	Electrophoretic mobility after mixing $\mu_e 2$, μmcm/Vs
MAA emulsion+AEM microgel	pH 3	−0.23 ± 0.00	+0.79 ± 0.08
	pH 7	−2.02 ± 0.04	−1.16 ± 0.16
	pH 9	−1.12 ± 0.24	−0.60 ± 0.02
AEM emulsion + MAA microgel	pH 3	+0.63 ± 0.13	−1.03 ± 0.14
	pH 7	+0.97 ± 0.16	−2.33 ± 0.04
	pH 9	−0.25 ± 0.02	−1.30 ± 0.05

Heptane dichloromethane mixture at 12:5, w/w.

Table S3. Characterization of the MAA and the AEM microgels in aqueous solution at different pH at 24 °C

		Hydro-dynamic radius R_h, nm	Diffusion coefficient D, $\mu m^2/s$	Electrophoretic mobility μ_e, μmcm/Vs	Amount of charge, mmol/g
MAA Microgel	pH 3	260 ± 7	0.92 ± 0.03	−1	0
	pH 7	381 ± 8	0.62 ± 0.02	−3.0	0.92
	pH 9	435 ± 31	0.54 ± 0.01	−1.5	1.13
AEM Microgel	pH 3	185 ± 2	1.30 ± 0.01	+0.8	0.30
	pH 7	218 ± 4	1.10 ± 0.02	+1.3	0.20
	pH 9	158 ± 2	1.52 ± 0.02	−0.2	0