# The polymerisation of emulsion droplets deformed using laser tweezers to create microscopic polymer particles

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## Introduction

In our previous experimental time[1] we were successful in demonstrating that micron-sized oil-in-water emulsion droplets could be deformed using multiple-beam laser tweezers. Altering the relative position of the optical traps deformed a heptane-in-water emulsion droplet into different geometric shapes. The deformations resulted from careful selection of an emulsion system in which the surface of the oil droplets experienced ultralow interfacial tensions. Through experimentation the most suitable emulsion system was composed of the surfactant Aerosol OT, heptane and solution of sodium chloride[2]. The optimum performance of the emulsion was at a temperature of 20°C in composition ratios approaching the phase boundary for microemulsion formation. The shapes could be readily formed with architectures defined by the number and spacing of the optical trapping positions (see Figure 1).

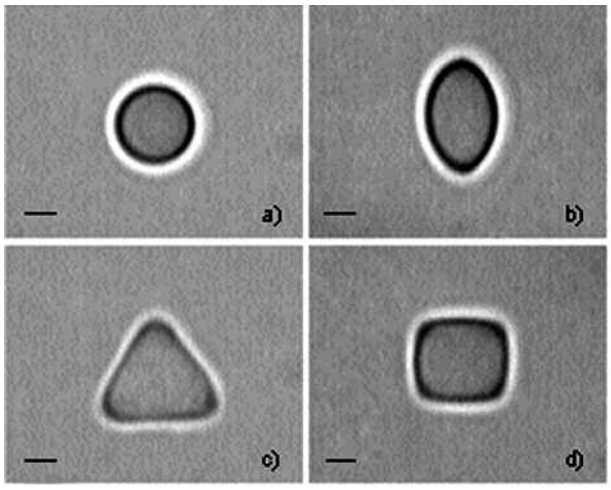


**Figure 1. Optically deformed droplets of oil in the emulsion formed from mixing heptane/AOT/NaCl solution. The triangular droplet uses three optical traps, one at each apex, to stretch out the originally spherical droplet. The square uses four traps in a similar method.**

We report the utilization of this droplet deformation phenomenon to investigate the fabrication of custom shaped polymer particles. This requires the formation of deformable emulsions containing monomers, instead of heptane, that can be polymerised using photointiation techniques. Such particles produced in-situ in the optical trapping environment could offer potential as novel microscopic building blocks in the construction of microstructures and waveguides.

## Experimental

The polymerisation process requires that a monomer, in combination with a compatible initiator, is incorporated into the emulsion formulation. The use of emulsions and microemulsions with monomers to facilitate polymerisation is a well known commercial process that has received much attention in literature[3,4]. The key feature for polymerising deformed droplets is that the interfacial tension at the surface is likely to significantly increase during polymerization. Therefore, if polymerisation is slow, the balance between interfacial tension and the laser trapping force may result in the droplet losing shape. To stop the droplet reverting to a sphere during polymerization it is beneficial to solidify the bulk before the surface, in order to preserve the low interfacial tension for as long as possible. Such a fast initiation and polymerisation process will be greatly assisted by the use of oil-soluble photoinitiators which are triggered by bathing the trapped droplet in a high flux of light using the large numerical aperture objective that is used for optical trapping. The type of polymerisation is analogous to that used for commercial suspension polymerisation applications where the locus of polymerisation is directed towards the monomer containing droplets.

The monomer-in-water emulsions were prepared from surfactant solutions contained 1mM AOT in the presence of a 0.1M NaCl. The solutions were made by addition of salt to a pre-prepared surfactant solution to prevent the solutions becoming too turbid. The monomer used in all cases was isobornyl acrylate (IBA) which is commonly used in inkjet printing technology. Irgacure 819 was selected as the photoinitiator and is from a commercial source. A cross-linking molecule was added in some of the formulations to assist shape retention. A combination of initiator and cross-linker were added to the monomer and the mixture was stored in darkened conditions to prevent premature photo-initation. The formulation was used either neat or pre-mixed with heptane and added at approximately 1%v/v to the surfactant solution.

The droplets were deformed as described previously by controlling the relative positions of multiple-beam optical traps. Polymerisation of the monomer is triggered when the droplet is irradiated with Ultraviolet (UV) light stimulating the photo- initiator to generate free-radicals. Ideally, polymerisation should be initiated over a period of less than 10 milliseconds. Typical light intensities for this process are in the order of 3 W/cm$^2$. The wavelength used for all single droplet polymerizations was 385 nm and this was produced using a tunable frequency doubled Coherent Mira-Verdi laser system. The laser beam (power 5mW) was

fibre delivered to the microscope and focussed onto the droplet to initiate polymerisation using the same high NA microscope objective lens that is used for trapping. Such focussing of the laser light will produce a flux over 1000 times greater than that normally used for photoinitiation, thus some attenuation of the light source was required. As the whole droplet should be irradiated simultaneously, a slightly narrower beam diameter than that used for optical trapping, was directed into the back aperture of the objective lens. The effect of narrowing the beam was to give a larger focal spot size.

## Results and discussion

***Deformation of monomer only droplets***

For optimum deformation of the emulsified monomer droplets the interfacial tension (IFT) at the oil-water surface needs to be ultra-low. With pure IBA system this occurred at around 25°C and heating the surfactant solution to 27-30°C prior to mixing resulted in good deformation once under the microscope. The ability to deform a given sample was very sensitive to sample preparation, particularly regarding temperature as ultra-low IFT is only observed over a couple of degrees centigrade. However, using IBA without additives we were successful in producing very fluid droplets. As expected no polymerization was observed with this system in the presence of UV light.

***Polymersation of monomer droplets***

Irgacure 819 was added to the monomer in concentrations of 1, 2 and 5 %w/w. The droplets were again easily deformed. Irradiation with UV light rapidly polymerised the droplets (less than 1 second) but they reverted to spherical shape on solidification. At higher initiator concentrations the larger droplets were distorted, lens-like at one end, flattened off at the other as shown in Figure 2.

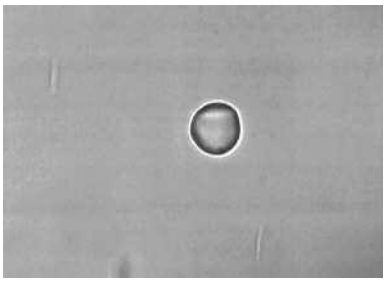

**Figure 2. An image of a distorted 10 micron diameter polymer particle after polymerizing an IBA monomer droplet containing Irgacure 819 photo-initiator.**

Addition of heptane to the monomer to give the formulation: 75 %w/w IBA, 25 %w/w heptane and 1 %w/w Irgacure 819 resulted in similar behaviour to that above but with slower reaction times.

***Addition of cross-linker***

Preparations were made with IBA, 1 %w/w Irgacure 819 and cross-linker at 2 %w/w, 3.5 %w/w, 5 %w/w and 23 %w/w concentrations. The IFT minimum for these systems is at a higher temperature, thus the surfactant solution was heated to 35-40°C to get good deformation. With the highest cross-linker concentration the droplets could not be deformed and with the lowest concentration the deformed droplets again reverted to solid spheres on polymerization. However, the 3.5 %w/w and 5 %w/w cross-linker formulation formed lozenge-shaped polymer particles from the deformed shape (see Figure 3). When repeating this polymerization using triangular shaped emulsion droplets the triangle shape could not be retained and again lozenge shapes were formed.

## Conclusion

The optimum formulation was IBA +1%w/w Irgacure 819 +5%w/w cross-linker added to the surfactant solution. This formulation gave both the desired deformation and polymerisation characteristics. However, with this system there appears to be limited shape retention of deformed droplets which appeared to take up the same solid shape regardless of the initial state of deformation. This observation suggests that the effect of the focal volume of the UV laser during polymerisation may outweigh that imposed the trapping force. De-focussing the UV beam gives the same results, suggesting that the final shape of the polymer is not aided by a slower rate of polymerisation (i.e. the same result was obtained with slower IBA/Heptane mixture),

On the other hand, the fact that not all the very deformable systems give this appreciable distortion in the polymer suggests that the process is rate dependant, and that the change in rate of initiation brought about by de-focussing is not significant. In all cases polymerisation is visually over in less than a second, but clearly a certain proportion of cross-linker is necessary to reach gel phase sufficiently rapidly. In our optimum formulation, it is possible that the IFT is slightly lower allowing for greater initial deformation and hence less relaxation of shape during polymerization.

The fact that we get appreciably distorted polymer only in very deformable cases suggests that IFT plays an important role, assuming that a sufficiently low interfacial tension is maintained during polymerisation for retention of a shape, albeit not the one we introduce. This is at least encouraging, as it proves that we can produce shaped polymer particles through the use of ultra-low IFT systems.

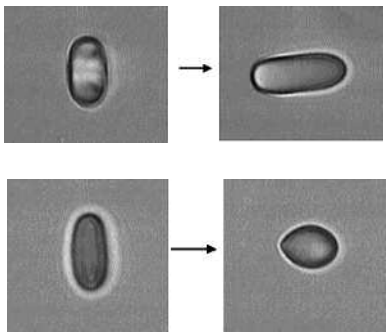

**Figure 3. Two examples showing images on the left of an optically deformed monomer emulsion droplets (IBA + 1%w/w Irgacure 819 + 5%w/w cross-linker) before being polymerized using photo-initiation at 385 nm. The resulting polymer particle is on the right.**

## References

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