# letter

## Comments on 'Formation of grains in a suspension of poly(vinyl chloride)' by J.-s. Zhao *et al.*

(*Received 11 March 1992*)

Recently Zhao *et al.* proposed a mechanism for the formation of poly(vinyl chloride) (PVC) by a suspension process other than the generally accepted 'classical' process of polymerization and subsequent precipitation of monomer swollen PVC particles in $\sim 150\,\mu m$ monomer droplets[1].

Zhao *et al.* propose that on agitation, liquid vinyl chloride disperses into water in the presence of dispersant as submicrometre droplets with a diameter of $\sim 0.7\,\mu m$ where polymerization then occurs. These droplets are then supposed to aggregate into PVC grains of $\sim 130\,\mu m$ diameter.

These authors were apparently unaware of our work published over 10 years ago on the direct microscopic observation of polymerizing vinyl chloride droplets[2]. In this work, specially constructed optical microscope pressure cells were employed which enabled us to sample stirred reactor polymerizations. Reactors from 3 l to > 15 000 l were sampled and in no case was anything other than the classical mechanism observed.

Non-agitated polymerizations were also studied. In this case a suspension of catalyst containing vinyl chloride droplets in water was prepared by shaking vinyl chloride, catalyst, dispersant and water in a suitable pressure tube and quickly transferring the contents to a microscope pressure cell. The catalyst level was adjusted so that the amount of polymerization which occurred during the mixing and transfer to the microscope cell was negligible. In the non-agitated case a unicellular PVC particle was formed which exactly corresponded to the presence of its parent droplet. The course of this transformation was documented on cine film. If the view of Zhao *et al.* is correct, such non-agitated polymerizations would be impossible.

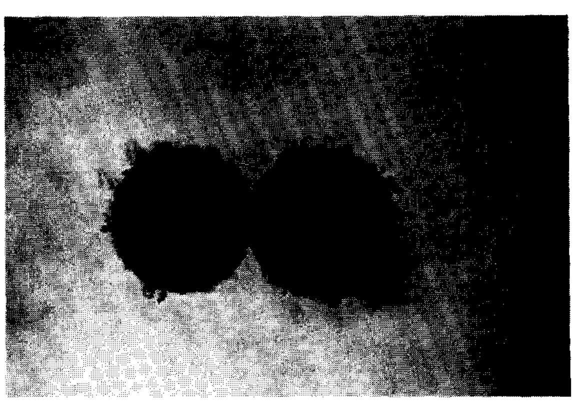

**Figure 1** Optical photomicrograph (bright field) of non-agitated $\sim 140\,\mu m$ polymerizing droplets of vinyl chloride in water. The interior of each particle is filled with 1–5 $\mu m$ grains of PVC in rapid Brownian motion

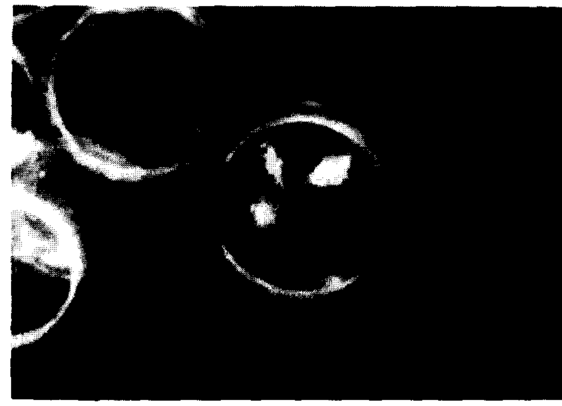

**Figure 2** Optical photomicrograph (dark field) of $\sim 200\,\mu m$ polymerizing droplets withdrawn from a stirred reactor. Note the presence of floc inside the centre droplet

The authors raise a number of points about the suspension polymerization of PVC and it is beyond the scope of this letter to discuss them. However, our work demonstrates that all of these issues, at least in the case of suspension polymerization as it is normally carried out, should be considered in light of the 'classical view' rather than the model proposed by Zhao *et al.*

In *Figure 1* is a photomicrograph of a non-agitated polymerizing droplet at 1–0.5% conversion. Each droplet is $\sim 140\,\mu m$ in diameter and the precipitated PVC grains inside the droplet can be clearly seen.

*Figure 2* is a dark field photomicrograph of polymerizing droplets of vinyl chloride withdrawn from a stirred reactor at a few per cent conversion. The interior of each droplet is filled with $\sim 1$–$5\,\mu m$ grains of PVC and some of these grains have flocculated to a larger size. The details of this flocculation process are given in ref. 2.

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REFERENCES

1 Zhao, J.-s., Wang, X.-q. and Fan, C.-g. *Polymer* 1991, **32**, 2674
2 Davidson, J. A. and Witenhafer, D. E. *J. Polym. Sci., Polym. Phys. Edn* 1980, **18**, 51

0032-3861/93/010222-01