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Letters

Observations of charge on nascent poly(vinyl chloride) particles in monomer

In the early stages of the polymerization of vinyl chloride (VCM) within monomer droplets, the precipitated polymer forms particles which are colloidally stable. We describe here an experiment to determine whether electrostatic charge resides on the surface of the particles.

A stainless steel pressure vessel, designed for measurement of surface and interfacial tensions of pendent drops of liquid VCM, was modified to enable an electrode to be introduced into a vinyl chloride drop. A gold-plated, needle-shaped electrode was insulated in a PTFE block, leaving only the tip protruding, and mounted in the top of the pressure cell. A 'D'-shaped steel plate (0.4 mm thick), with a 3 mm hole drilled through, was mounted 3 mm below the electrode tip. Water and liquid VCM were introduced into the cell through a glass capillary tube (0.5 mm bore, 6 mm O.D.) fitted to a non-return ball valve in the base of the cell. The electrode, glass capillary and hole in the plate were vertically aligned, the plate being 4.5 mm above the tip of the capillary. All steel surfaces within the cell had previously been gold-plated.

The cell was first filled with water until the level was above the top of the observation windows, then pressurized with nitrogen (~13 bar). Liquid VCM, containing 0.2% w/v dicetyl peroxydicarbonate as initiator, was then admitted, forming pendant drops at the capillary tip before detaching and rising to the water surface. By varying the drop size and rate of admission of VCM, it was possible to pass drops through the hole in the plate and trap them between the plate and electrode. In this way an isolated conical drop (volume ~0.03 cm^3) was held between the plate and electrode tip as shown in *Figure 1*. Polymerization was initiated within this drop by heating the cell in a current of hot air. After 90 min, when the cell temperature was 48°C, the drop became turbid and heating was stopped. Polaroid photographs of the drop were taken throughout the experiment (magnification x 5) and, 10 min after heating stopped, a photograph showed that the suspended PVC particles had sedimented sufficiently to leave a clear layer of monomer at the top of the drop. Potential differences of ±1.5 V were then applied between the electrode and the plate and movement of the dispersion/monomer boundary

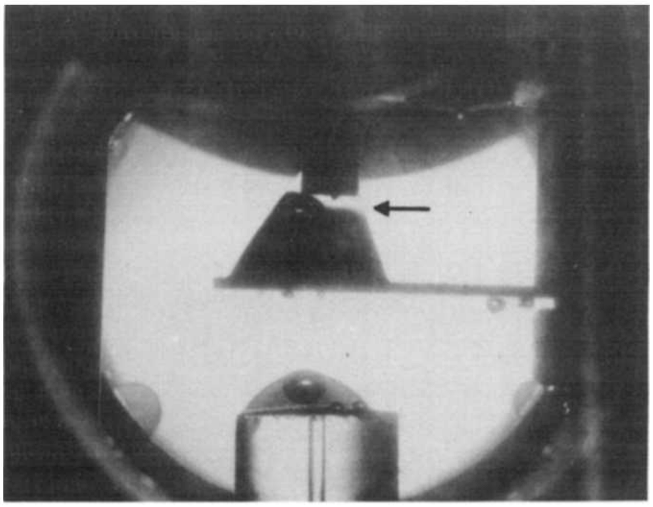

Figure 1 Monomer droplet held between electrode tip and plate in an aqueous medium

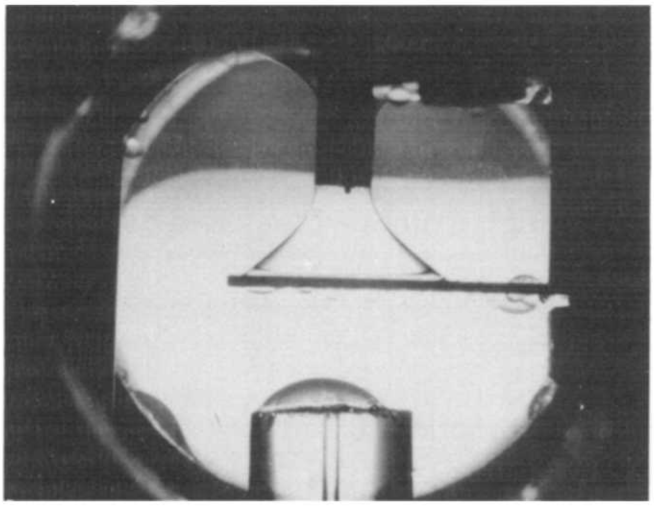

Figure 2 Movement of dispersion/monomer boundary (indicated by arrow) from electrode tip on application of −1.5 V to the electrode tip

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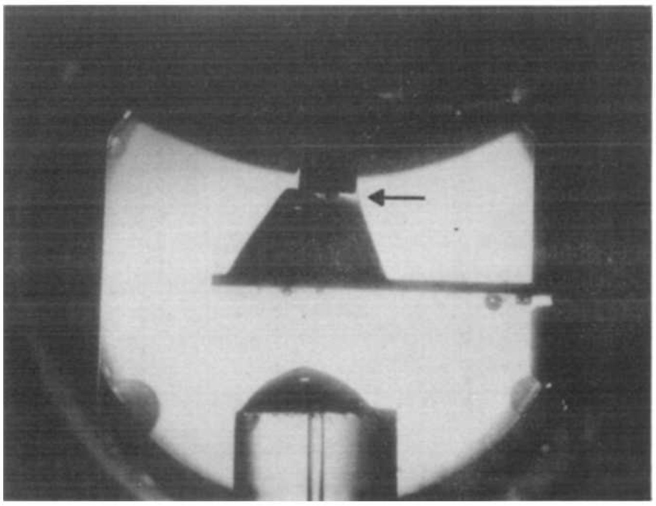

Figure 3 Movement of dispersion/monomer boundary (indicated by arrow) towards the electrode tip on application of +1.5 V to the electrode tip

was observed as demonstrated by comparing *Figures 2* and *3*. It should be noted that the left hand side of the dispersion/monomer boundary in the conical monomer drop shown in *Figures 2* and *3* is obscured by a vapour-bubble of VCM.

The polarity of the applied field and the direction of movement of the dispersion/monomer boundary showed that the PVC particles carried a negative charge. However, uncertainty in the magnitude of the electric field between the electrodes meant that no quantitative estimate of the electrophoretic mobility of the PVC particles in monomer could be made.

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Electrophoresis of poly(vinyl chloride) dispersed in vinyl chloride monomer

Introduction

Bulk poly(vinyl chloride) (PVC) formed by initiation in liquid vinyl chloride monomer (VCM) appears to consist of aggregates of small polymer particles. The size of the aggregates and constituent particles greatly affects the porosity of the bulk material and so knowledge and control of the stage in the polymerization at which aggregation occurs is important. It has been suggested that the polymer particles, before aggregation, might be electrically charged[1] and that the colloidal stability of these so-called primary particles might be affected by the magnitude of particle charge in a manner predicted by colloidal stability theory. We describe here an examination of the electrophoresis of PVC primary particles dispersed in liquid VCM.

Experimental

We have constructed an electrophoresis cell which can withstand the pressures of about 10 atm necessary to liquefy VCM at temperatures up to 350K. The cell, shown in *Figure 1*, is constructed of quartz. Pt wire electrodes are inserted through glass/metal seals. The lower tube, in which particle electrophoresis was examined, is a cylindrical capillary of 2.6 mm internal diameter. The front and back external faces are ground flat to reduce optical distortion. The two larger diameter electrode compartments joined to the lower tube are also connected by an upper cross tube. Each electrode compartment is fitted with a side arm to which ball valves can be attached and through which the cell can be filled or emptied.

Using apparatus described elsewhere[2] approximately 5 cm^3 of VCM was polymerized to about 4% conversion in a pressure test tube and a small sample of this dispersion was added to about 6 cm^3 of VCM in the electrophoresis cell. This reduction of the initial particle concentration by a factor of about 100 was necessary to give a low enough particle concentration in the electrophoresis cell for examination by ultramicroscopy.

Particle electrophoresis was observed using an electrophoresis apparatus (Rank Bros., Cambridge) in which the quartz cell was positioned vertically in a thermostat bath. On application of a potential gradient of about 16 V/cm, the particle velocity was determined by noting the time taken for particles to travel a given distance as indicated by a calibrated graticule in one microscope eyepiece.

The observed velocity, ν_{obs}, for particle electrophoresis in a circular cross section capillary is given by:

$$\nu_{obs} = \nu_e + \nu_{eo}(2(r/a)^2 - 1)$$

where ν_e is the electrophoretic velocity, ν_{eo} the electro-osmotic velocity, r the distance from the centre of the cell to the point of observation and a the internal radius of the capillary. A plot of ν_{obs} against $(r/a)^2$ should be linear for electrophoresis about the axis of the capillary and at the stationary levels ν_{obs} is equal to ν_{eo} when $(r/a)^2$ is equal to 0.5. An optical correction is necessary for locating a given level within the cell because of curvature of the inner wall of the capillary. The usual correction for a Mattson type cell[3] has been used[4].

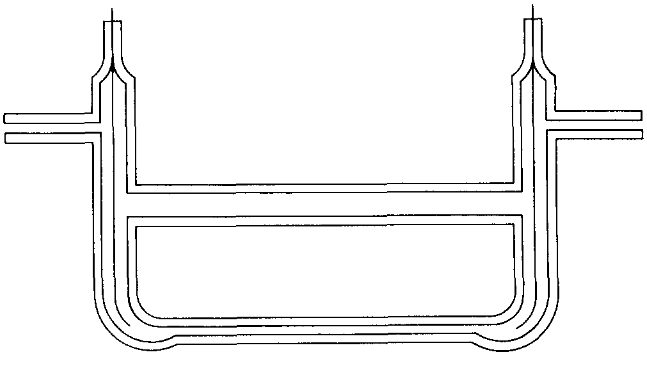

Figure 1 Electrophoresis cell

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