Primary particle stability in bulk polymerization of vinyl chloride at high ion strength

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Tetrabutyl ammonium tetrafluoroborate and tetrabutyl ammonium chloride dissociate completely in vinyl chloride (VCM). These salts, when added to colloidal dispersions of PVC primary particles in VCM prepared by bulk polymerization, cause the particles to flocculate, showing that the primary particles were electrostatically stabilized. When bulk polymerizations were carried out in the presence of the same quarternary ammonium salts, smaller primary particles were obtained than in additive-free polymerizations. Addition of tetrabutylammonium tetrafluoroborate to a suspension polymerization increased the porosity of the resin.

(Keywords: poly(vinyl chloride); primary particles; particle stability; electrical conductivity)

INTRODUCTION

In bulk and suspension polymerization of vinyl chloride monomer (VCM) the polymer precipitates in the form of small particles as soon as polymerization starts. This is due to the low solubility of the polymer in VCM. The smallest stable particles observed have a size of about 100 nm, and are known as primary particles. These particles are colloidally stable for only a limited period after their formation. The stability of the primary particles decreases during particle growth[4,7] and the particles agglomerate when they reach a certain size. The point at which agglomeration begins depends on the reaction conditions[1,2]. Particle growth is rapid during the period of colloidal stability, but very slow after agglomeration[3]. Thus, the presence of small, agglomerated primary particles indicates an early agglomeration of particles with a low stability.

Several studies have shown that the primary particles are negatively charged[4,5], indicating that perhaps the particles are electrostatically stabilized. Electrostatically stabilized particles would be sensitive to electrolytes dissolved in the monomer. A separate study[6] showed that electrolytes present as impurities in the surfactant Span 20 may destabilize the primary particles. The purpose of this paper is to further explore the relationship between particle stability and electrolyte concentration.

EXPERIMENTAL

The polymerization experiments were made in a 200 ml glass-walled reactor with an enamelled stainless steel top and bottom. The conversion, particle size and particle number were measured as described in previous papers[2,3]. For measurements of the electrical conductivity of VCM two cylindrical electrodes were mounted inside the reactor. Each electrode had a surface area of about 80 cm^2. The distance between the electrode surfaces was 3 mm. The cell constant was determined by comparison with a calibrated cell and was found to be 0.0024 cm^{-1}. The conductivity was measured at 1 kHz with a Metrohm Herisau conductimeter E527, an instrument which automatically compensated for the large cell capacitance, enabling conductivity measurements of down to 2.4 nS/cm to be done.

Vinyl chloride, kindly supplied by Kema Nord Plast AB (presently Norsk Hydro Plast AB), was distilled twice and the permanent gases were vented before use. The tetrabutyl ammonium tetrafluoroborate (Bu_4NBF_4) and tetrabutyl ammonium chloride (Bu_4NCl), were used as received from Fluka AG. They had a moisture content of less than 3%.

RESULTS AND DISCUSSION

Dissociating salts

The quarternary ammonium salts Bu_4NBF_4 and Bu_4NCl dissolved readily in VCM. The conductivity of the VCM solutions of these salts are given in *Figure 1* as the difference between the conductivity of the salt solutions (k) and that of pure VCM as measured before addition of the electrolytes (k_0). In this way, variations in the pure VCM conductivity, which ranged from 2.4 nS/cm to 11 nS/cm in the different experiments, were compensated for. The fact that plots of $\ln(c)$ vs. $\ln(k-k_0)$ gave lines with unit slopes shows that the salts were completely dissociated.

The chloride salt had a lower conductivity than the fluoroborate salt. This was unexpected, since the smaller Cl^- ion should have a higher mobility and thus a higher conductivity than the larger tetrafluoroborate ion. The low mobility of the Cl^- ion must be due to a better solvation of the Cl^- ions.

The conductivity of Bu_4NBF_4 deviates from linearity at concentrations below 0.3 $mmol\,l^{-1}$ (*Figure 1*). The deviation at these low concentrations was reproducible. At a concentration of 50 $\mu mol\,l^{-1}$, the difference between

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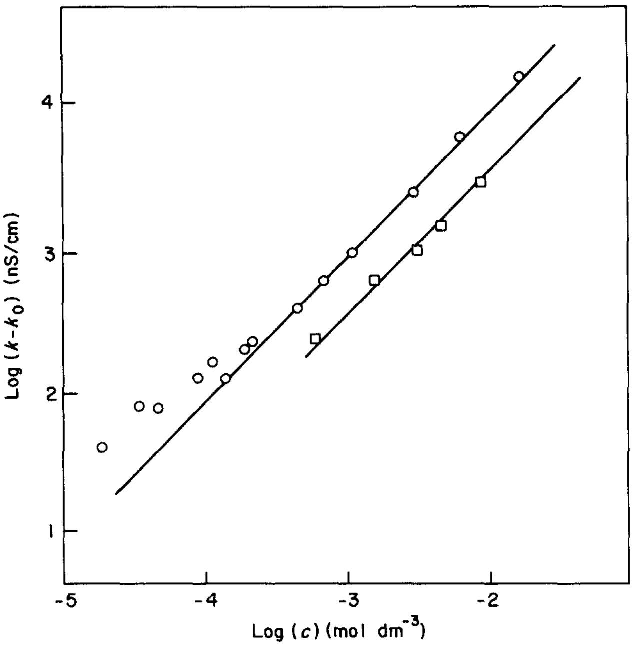

Figure 1 Electrical conductivity of VCM containing (○) Bu_4NBF_4 and (□) Bu_4NCl

the extrapolated line and the measured conductivity was 49 nS/cm, whereas, at the lowest concentration, about 15 μmol l^{-1}, the difference was 28 nS/cm. In other words, the observed conductivity at 15 μmol l^{-1} was more than 2.5 times that corresponding to the linear correlation. This deviation from a linearity at low concentrations is not understood.

The electrical conductivity of pure VCM, which averaged about 8 nS/cm, must be due to the presence of ionic species in the monomer. Extrapolating the conductivity values in *Figure 1* to that of the pure VCM indicates that the concentration of dissociated electrolytes in the pure monomer was about 1 μmol dm^{-3}, assuming the same ionic mobilities as that of Bu_4NBF_4. The ionic species in the pure monomer probably were by-products formed during the monomer synthesis. Tests with monomer dried over P_2O_5 showed no change in conductivity, indicating that the conductivity of VCM is not related to the monomer water concentration.

Quiescent bulk polymerizations

VCM was polymerized to about 0.1% conversion, at 40°C in a PVC coated glass flask without agitation, using dicetylperoxidicarbonate as initiator. The flask was then cooled to 20°C. The primary particles formed remained colloidally dispersed and stable in the VCM phase, provided that the flask was not shaken.

Addition of a Bu_4NBF_4 solution to the dispersed primary particles in the flask (at 20°C) initiated a fast flocculation of the particles. The critical flocculation concentration was found to be between 7 and 10 mmol l^{-1} for this 1:1 electrolyte. The appearance of a critical flocculation concentration confirms that the particles were electrostatically stabilized.

Agitated bulk polymerizations

Polymerization of VCM in the presence of Bu_4NBF_4 resulted in the formation of small primary particles (*Table 1*). Small primary particles are obtained when the particles agglomerate at low conversions, which occurs when the particles are destabilized[3]. The fact that small particles were obtained during polymerization in the presence of quartenary ammonium salts is further proof that the particles were destabilized by addition of electrolyte. The destabilization was effective at both levels of agitation.

Addition of Bu_4NCl to bulk polymerizations also caused a decrease in the primary particle size (*Figure 2*), in this case from 0.18 μm to 0.13 μm on addition of 0.02 wt% of the salt. A further increase of the salt concentration had little effect on particle size. A sharp decrease in particle size during polymerization in presence of dissociated electrolytes should be expected, since electrostatic stabilization is very sensitive towards the ionic strength[9]. However, simple electrostatic theory does not explain why a further decrease in particle size did not occur when the electrolyte concentration was increased above 0.02%. Possibly, a stabilizing mechanism besides the electrostatic one plays a role in the formation of PVC primary particles.

It has been suggested that the stabilizing particle charge is due to absorption of Cl^- ions[5,7,8]. According to this suggestion, substances which dissociate into Cl^- ions in the monomer should increase the particle charge. Concentrations of Cl^- ions that are large compared to the normal level, but much smaller than that required to coagulate the primary particles, should produce primary particles with increased stability. This increase in stability should result in the formation of larger primary particles. However, at the lowest Cl^- ion concentration tested, 10 nmol l^{-1}, which should fulfil the above requirements, no increase in particle size was observed. The absence of a stability increase in this experiment implies that the particle charge was not increased by adding chlorine ions. Therefore, it is not clear that the absorbtion of Cl^- ions contributes to particle stability.

The electrostatic nature of the particles was also evinced by the string structure of agglomerated primary

Table 1 Effect of Bu_4NBF_4 in bulk polymerization of VCM on primary particle size (*d*) and number of particles formed (*N*)

Bu_4NBF_4 (% wt)	Agitation* (m/s)	Conversion (%)	*d* (μm)	$N \times 10^{-14}$ (mol^{-1})
0.00	0.4	1	0.32	0.25
0.02	0.4	1	0.25	0.65
0.20	0.4	1.4	0.10	9.00
0.00	1.5	3	0.18	3.9
0.02	1.5	3	0.12	12.0

*Tip speed of anchor agitator

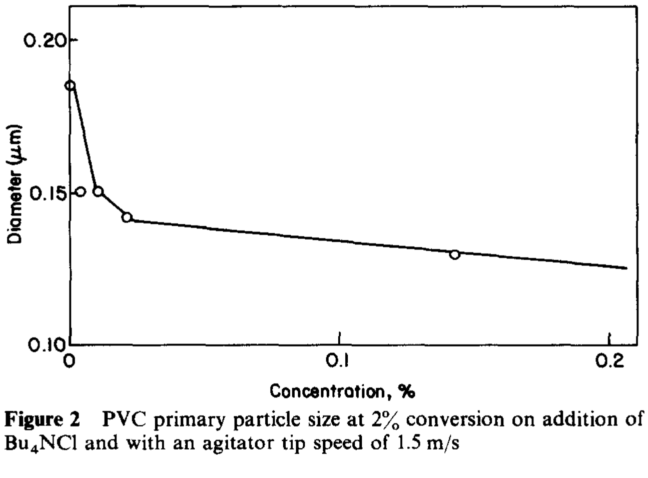

Figure 2 PVC primary particle size at 2% conversion on addition of Bu_4NCl and with an agitator tip speed of 1.5 m/s

particles, observed in agglomerates formed during polymerization at high agitation rates (*Figure 3*). The strength of the particle repulsive force depends on the size of the agglomerating particles[7]. If the agitation is high the particles agglomerate when they are relatively small in size and still posess a high repulsive electric potential. If two small particles agglomerate, their electric fields are superimposed. The electric field around a particle doublet has a minimum strength at its two end points. A third particle approaching the doublet would therefore tend to agglomerate at one of these points, forming a triplet. By repetition of this process strings of agglomerated primary particles would be formed, like those shown in *Figure 3*.

At slow agitation, the particles will not agglomerate until they reach a larger size, at which their repulsive potential has decreased to a very low value. In this case the superimposed electric field around a doublet would be less asymmetric and much less able to exert a directing influence on agglomeration as in the corresponding case with small particles. Therefore, the build-up of the agglomerates will to a greater extent, be determined by the van der Waals attraction forces, which would favour densely packed structures. As shown in *Figure 4*, a structure of higher packing density and less string-like formations was produced at low agitation speed.

Suspension polymerizations

The relationship between particle size and final resin porosity has been discussed on many occasions. It has been suggested that smaller primary particles would lead to higher porosity, although no experimental material supporting this assumption has been published. In a recent work on bulk polymerization of VCM it was found that the primary particles decreased in size on addition of the nonionic surfactant Span 20[3]. It is possible that the reported effect of Span 20 in suspension polymerization as a porosity increasing agent is caused by a particle size effect.

Suspension polymerizations with addition of 0.02 g and 0.2 g of Bu_4NBF_4, per 100 g of VCM, gave resins with increased porosity (*Table 2*). At 0.2% Bu_4NBF_4 the porosity increased by 13%. Also, addition of the salts was followed by an increase in the grain size and gave a broader grain size distribution.

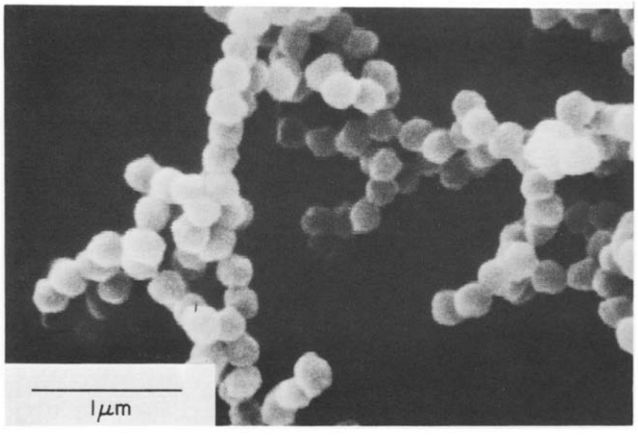

Figure 3 Agglomerated PVC primary particles as observed at 2% conversion, in polymerization experiments with high agitator speed (tip speed 1.5 m/s)

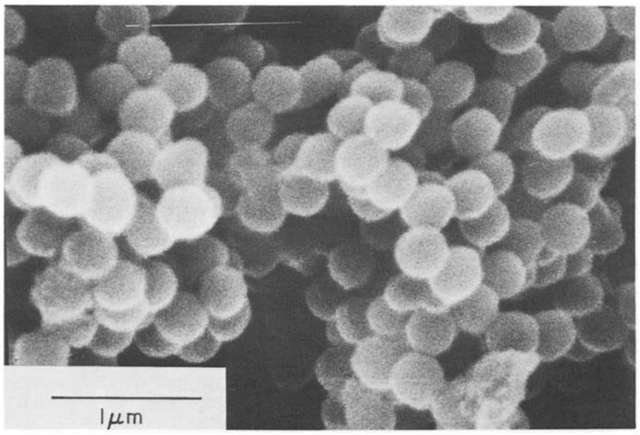

Figure 4 Agglomerated PVC primary particles as observed at 0.5% conversion, in polymerization experiments with no agitation

Table 2 Properties of fully converted S-PVC on addition of Bu_4NBF_4

Concentration (%)	Grain size Average (μm)	Grain size Standard deviation	*K*-value	Porosity (%)	Bulk density (kg/m^3)
0.0	120	1.25	67.4	21.4	538
0.02	135	1.40	68.0	23.5	550
0.20	150	1.43	68.0	24.7	532

PVC resin porosity would partly be determined by the forces in the interface between water and monomer as water starts to replace the monomer in the porous system of the grain. The entry of water into the grain structure requires interfacial work. This work is determined by the interfacial tension and the pore size. The pore filling process will give a porosity decreasing pressure gradient at the interface between water and free monomer.

Increasing the monomer ionic strength will destabilize the particles in a suspension polymerization in the same way it does in bulk polymerizations. The destabilized particles will agglomerate at lower conversion and at smaller particle sizes. The increased porosity obtained in suspension polymerization at high ionic strength indicate that an early agglomeration of smaller primary particles promotes formation of porous PVC grains. Whether this is due to the formation of a stronger internal structure, or if the destabilized particles build a skin at the water VCM interface that is easily penetrated by water is not known.

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REFERENCES

1 Boisell, J. and Ficher, N. *J. Macromol. Sci. Chem.* 1977, **A11**, 1249
2 Törnell, B. E. and Uustalu, J. M. *J. Vinyl. Technol.* 1982, **4**, 53
3 Törnell, B. E. and Uustalu, J. M., to be published in *J. Appl. Polym. Sci.*
4 Wilson, J. C. and Zichy, E. L. *Polymer* 1979, **20**, 264
5 Davidson, J. A. and Witenhafer, D. E. *J. Polym. Sci. Polym. Phys. Edn.* 1980, **19**, 51
6 Törnell, B. E. and Uustalu, J. M., to be published
7 Spiers, R. M. Thesis, University of Edinburgh, UK, 1980
8 Rance, D. G. and Zichy, E. L. *Polymer* 1979, **20**, 266
9 Törnell, B., Uustalu, J. and Jönsson, B., to be published
10 Nilsson, H., Silvegren, C. and Törnell, B., to be published in *J. Vinyl. Technol.*
11 Wolf, F. and Schüssler, I. *Plast. Kautsch.* 1971, **18**, 492