γ-Radiolysis Investigation of the Effect of Electrosteric Stabilizers in Emulsion Polymerisation.

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INTRODUCTION

An emulsion polymerisation typically consists of two phases: the continuous aqueous phase, and the discreet organic phase, which comprises of monomer droplets and latex particles.[1] This system is stabilised by some form of surfactant. While polymerisation mainly occurs in the latex particles, the events which initiate polymerisation usually occur in the aqueous phase. Therefore, the transfer of radical activity from the aqueous phase to the organic phase (otherwise known as entry) is important in the kinetics of polymerisation. Likewise, transfer of radicals from the latex particles to the aqueous phase (exit), is important as a means whereby polymerisation in the latex particle ceases.

These entry and exit events have been studied for systems stabilised by electrostatic stabilisers (e.g. SDS, AMA80), and models for these events put forward. The current model for entry,[2] states that initiator decomposes in the aqueous phase, undergoes the initial propagation step with a monomer, and then polymerizes to a critical degree of polymerization (z) where the radical becomes surface active on the latex particle and enters the particle. It is assumed that both the initial propagation step and the entry of a radical of length z are not rate determining. The model for exit, the transfer-diffusion model[3], states that radical activity is transferred from the propagating polymeric radical to a monomer by hydrogen abstraction. This monomeric radical can either propagate in the particle or diffuse into the aqueous phase.

Experiment studies of entry and exit rate coefficients for electrostatically stabilised systems have show good agreement with these models.[4] However, studies which involved other types of surfactant, such as surface-active initiators, known as "inisurfs", have exit rate coefficients of approximately an order of magnitude below that which is expected for particles of that size.[5]

EXPERIMENTAL

This study utilises seeded emulsion polymerisations. By this method, the particle number and particle size can be chosen, and complex particle formation kinetics can be disregarded. Two electrostatically stabilised styrene latices were grown, of 24 nm and 44 nm particle radius. A portion of the these latices was reserved for kinetic studies. Poly(acrylic acid), an electrosteric stabiliser, was absorbed onto the surface of the latex particles as a second stage procedure, forming electrosterically stabilised latices.

Dilatometry was used to measure the conversion rate: the steady state rate with chemical initiator and relaxation from steady state in a system initiated by γ radiolysis, can be used to obtain the exit rate coefficient. Given the exit rate coefficient and the steady state rate of polymerisation, entry rate coefficients can be obtained.[1]

RESULTS AND CONCLUSIONS

Some results are shown below for the 24 nm radius particles. Entry and exit rate coefficients were obtained for both electrostatically and electrosterically stabilised latices, for

pH 4 and pH 7, and with increased ionic concentration.

It was observed that the measured entry and exit rate coefficients electrostatically stabilised latices agreed well with the rate coefficients predicted by the models, especially at pH 4 and pH 7. However, the measured values of the entry and exit rate coefficients were significantly decreased in electrosterically stabilised systems. The largest decrease was noted at pH 7, where the electrosteric stabilized was deprotonated. As pH decreased to pH 4, the exit and exit rate coefficients increased. It was hypothesed that this increase was associated with the electrosteric stabilizer becoming more compressed. Likewise, when the electrosteric stabilizer was compressed through the addition of sodium chloride, an increase in entry and exit rate was noted.

These observations are consistent with the existance of a "hairy layer" of electrosteric stabiliser, which slows aqueous-phase diffusion. The effects of change of pH and ionic strength are consistent with this hypothesis.
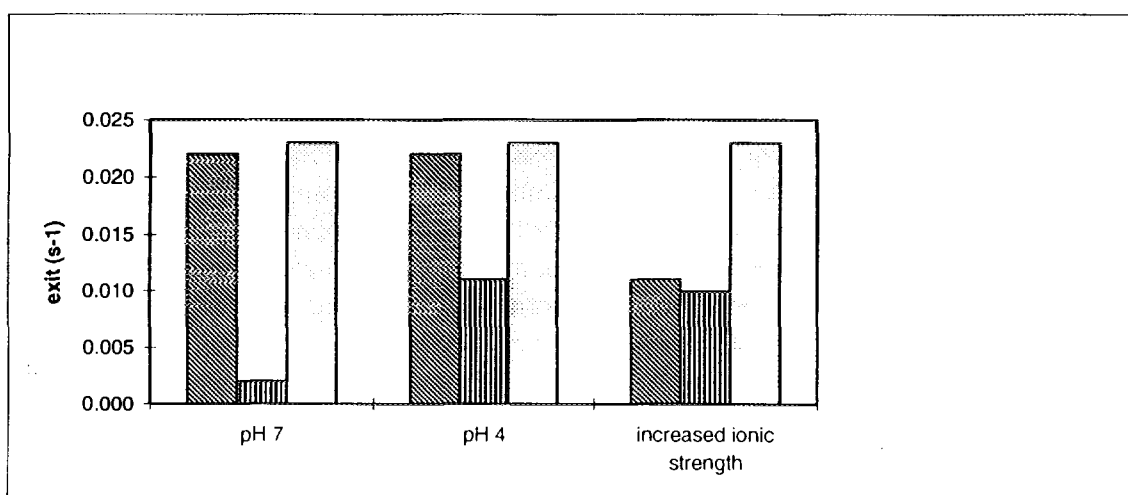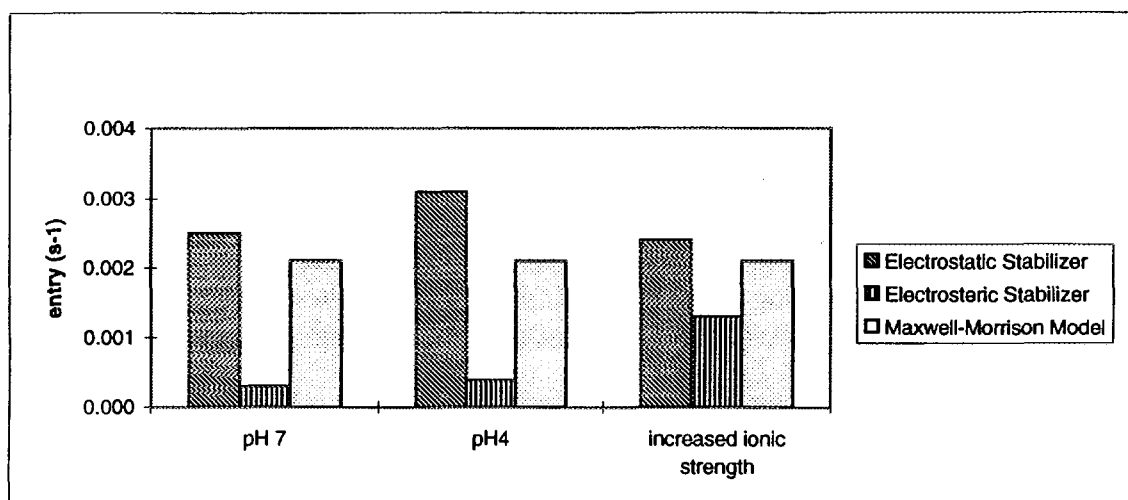
[1] *Emulsion Polymerisation, A Mechanistic Approach;* R. G. Gilbert; Academic Press; London, 1995
[2] Maxwell, I.A.; Morrison, B. R., Napper, D. H.; Gilbert, R.G.; *Macromolecules.* 1991, *24*, 1629
[3] Ugelstad, J.; Hanses, F. K.; *Rubber. Chem. Technol.* 1976, *49*, 536
[4] Hawkett, B. S..; Napper, D. H.; Gilbert R. G., *J. Chem. Soc. Faraday Trans. I* 1980, *76*, 1323
[5] Kusters, J.M.; Napper, D. H.; Gilbert, R. G., German, A. L.; *Macrocmolecules,* 1992, *25*, 7035