Non-aqueous polystyrene dispersions: steric stabilization by partially hydrolysed poly(vinyl alcohol) in methanolic media

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(Received 20 April 1994; revised 1 August 1994)

Near-monodisperse polystyrene particles have been produced by dispersion polymerization in the presence of partially hydrolysed poly(vinyl alcohol) (35 mol%) as steric stabilizer in methanolic media. Control of mean particle size in the range 0.5–3.0 μm is demonstrated by modifying the solvency of the diluent for polystyrene which is presumed to influence the nucleation mechanism for particle formation.

(Keywords: polystyrene; dispersion polymerization; steric stabilization)

Introduction

Polymer particles dispersed in organic media are prevented from flocculation by surrounding each particle by a surface layer of adsorbed polymeric stabilizer. The preparation and properties of particles of acrylic and vinyl polymers sterically stabilized in hydrocarbons by copolymers are well documented[1].

Over the last decade, attention has been directed to the formation of monodisperse polymer particles in alcohol-based media. An important advance was reported by Almog *et al.*[2] who employed a polymeric steric stabilizer, e.g. poly(*N*-vinyl pyrrolidone), in conjunction with a cationic surfactant as costabilizer, e.g. methyl tricapryl ammonium chloride. Tseng *et al.*[3] and Yu *et al.*[4] extended this work with poly(*N*-vinyl pyrrolidone) as steric stabilizer by considering other costabilizers based on anionic and non-ionic surfactants, long-chain alcohols and comonomers. The necessity of using a costabilizer has been debated[5,6], and it appears that uniform polymer particles can be produced without costabilizer as long as the concentration of polymeric steric stabilizer is not too low[7]. This latter conclusion is in line with studies of cellulosic derivatives, in particular hydroxypropyl cellulose, in alcoholic media without costabilizer[8–10].

Previous studies of non-aqueous polymer dispersions in hydrocarbon media from these laboratories have considered the properties of the adsorbed surface layer in terms of the structure of an adsorbed diblock copolymer consisting of well characterized anchor and stabilizing blocks[11–14]. For studies of polystyrene dispersions in methanol, attention was therefore directed to partially hydrolysed poly(vinyl alcohol) since chains produced under alkaline hydrolysis conditions have a blocky structure[15]. A range of adsorbed steric stabilizer structures is therefore possible, dependent on level and method of hydrolysis and on the lengths of sequences of vinyl alcohol and vinyl acetate units. The only reference to partially hydrolysed poly(vinyl alcohol) (18 mol%) in dispersion polymerizations of styrene was by Almog *et al.*[2], who appeared to indicate the necessity for a cationic costabilizer to be present in order to achieve stability. In this initial communication, we report the method of radical dispersion polymerization of styrene in methanol in the presence of partially hydrolysed poly(vinyl alcohol) (35 mol%), and also how particle size may be controlled by adding diluents to the methanol dispersion medium.

Experimental

Chemicals. Azobisisobutyronitrile (Aldrich) as initiator was recrystallized from methanol before use. Styrene monomer (Aldrich) and methanol (Carless Solvents) were distilled before use. Glycerol (Fisons Scientific) and ethanol with benzene (0.4%) (Carless Solvents) were used as received.

Partially hydrolysed poly(vinyl alcohol) (35 mol%) was supplied as a solution under the trade name Alcotex 359B (Harlow Chemical Company Ltd). This solution consisted of polymer (26% by weight), methanol (65%) and methyl acetate (9%) and was used as received.

Dispersion polymerization. Non-aqueous dispersions of polystyrene were prepared using methods well established in these laboratories[11–14]. The solution of Alcotex 359B was added to methanol or to the liquid mixture (methanol/glycerol or methanol/ethanol) forming the dispersion medium. Monomer was dissolved in the diluent with stirring, initiator was added, and the reactor was heated to 340 K after introducing a flow of nitrogen. Polymerizations were performed for 24 h.

In order to remove unconverted monomer, unadsorbed steric stabilizer and initiator residues from the particles as-prepared, dispersions were subjected to redispersion cycles. Particles were sedimented with an LKB Ultrospin centrifuge operating at 15 000 rev min^{-1} for 20 min. The clear supernatant fluid was carefully removed from above

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0032-3861/94/24/5366–03

the sedimented particles and was then replaced with fresh methanol. The particles were redispersed, and the sedimentation–separation–redispersion procedure repeated five times.

Particle characterization. Transmission electron microscopy (TEM) was used to determine particle size, shape and size distribution. Samples were prepared by placing two or three drops of the diluted dispersion (~0.1% w/v polymer content) directly onto a carbon-coated copper grid and evaporating to dryness. Samples were examined at suitable magnifications using a JEOL 100 cx transmission electron microscope with scanning transmission facilities, calibrated with a grid having 2160 lines mm^{-1}. Mean particle diameter and distribution were estimated by direct measurement of the individual particles on the negatives taken for each dispersion. Particle shape was also assessed by scanning electron microscopy (SEM) with a Cambridge Stereoscan 360 instrument equipped with a Link AN1000 energy dispersive spectrometer and a Microspec WDXZA wavelength dispersive spectrometer. Samples were prepared by placing a drop of diluted dispersion onto a glass cover-slip glued to an aluminium SEM stub, evaporating to dryness and sputtering with gold.

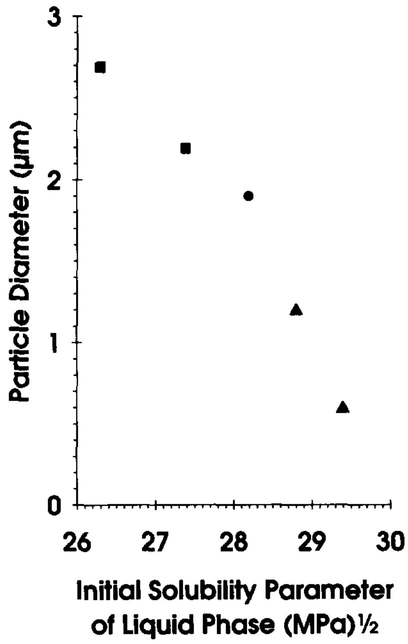

Figure 2 Dependence of mean particle diameter on the polarity of the liquid phase (diluent and monomer) at the start of dispersion polymerization: ●, methanol as diluent; ■, methanol/ethanol as diluent; ▲, methanol/glycerol as diluent

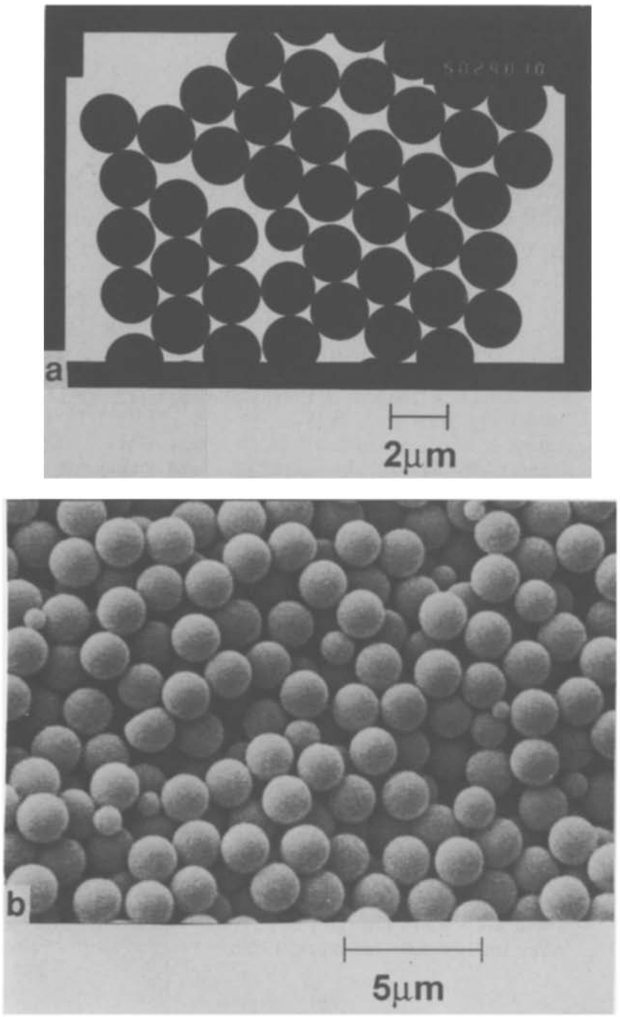

Figure 1 TEM (a) and SEM (b) micrographs of polystyrene particles produced by dispersion polymerization with methanol as diluent

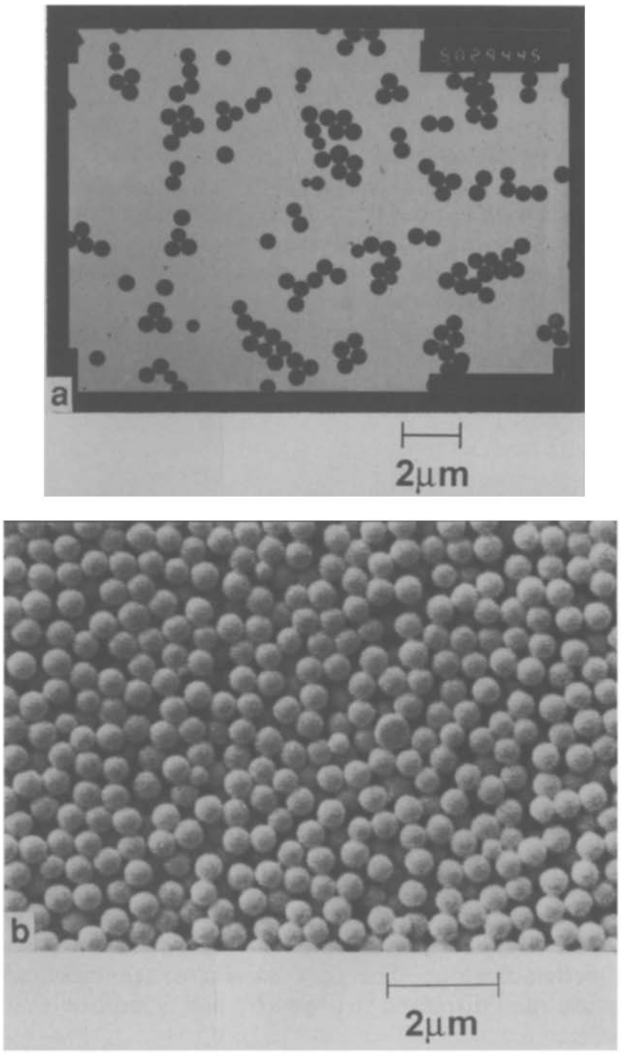

Figure 3 TEM (a) and SEM (b) micrographs of polystyrene particles produced by dispersion polymerization with methanol/glycerol (50:50 w/w) as diluent

Results and discussion

Typical dispersion polymerizations involved styrene monomer (16.8% w/w) and initiator (0.5% w/w) in methanol. Micrographs for particles produced at a steric stabilizer concentration of 3% w/w in methanol are shown in *Figure 1*. Dispersion polymerizations with steric stabilizer at a concentration of 1.5% w/w produced significantly larger particles and increased polydispersity. This observation can be attributed to the coalescence of some particles at lower concentrations of steric stabilizer because of incomplete surface coverage. The size distribution in *Figure 1* is very close to monodisperse with a mean particle diameter of 1.9 μm. An excess steric stabilizer concentration beyond 3% w/w did not provide marked changes in particle size, and a dispersion produced with 5% w/w steric stabilizer had a mean particle diameter of 1.7 μm.

A series of dispersion polymerizations was performed with diluents both more and less polar than methanol. All the other reaction conditions were maintained according to the method for preparing the particles displayed in *Figure 1*. Theories of particle formation indicate that larger particles are formed as the solvency of the diluent for the growing polymer chains increases due to the precipitation of a smaller number of nuclei at the start of dispersion polymerization[1]. Experiments to confirm the influence of solvency of dispersion medium for polystyrene were performed with mixtures of methanol/glycerol and methanol/ethanol as diluents. Compositions of liquid mixtures were selected such that the partially hydrolysed poly(vinyl alcohol) was soluble in the initial mixture of diluent and monomer (held at a fixed concentration of 16.8% w/w) at the reaction temperature. Since it is presumed that particle size is determined by the number of nuclei formed at the start of dispersion polymerization, solvency for polystyrene was judged in terms of the initial liquid composition of diluent and monomer. Solvency for polystyrene was represented in terms of liquid polarity as defined by the solubility parameter $\delta/(\mathrm{MPa})^{0.5}$. The calculation of δ for a liquid mixture was performed according to the equation[10]:

$$\delta = (\Sigma v_i \delta_i^2)^{0.5} \qquad (1)$$

in which v_i is the volume fraction of each component taking values of δ_i 19.0 (styrene), 29.7 (methanol), 33.8 (glycerol), 26.0 (ethanol) and 19.6 (methyl acetate)[16]. The diluent compositions for methanol/glycerol and methanol/ethanol were 50:50 and 75:25 w/w. The dependence of mean particle size on the solvency of the initial liquid phase for polystyrene at the start of dispersion polymerization is displayed in *Figure 2* and confirms the expected behaviour. Particle size distributions were near-monodisperse, as may be judged from the micrographs in *Figure 3* for particles produced in a dispersion medium with the lowest solvency for polystyrene. The introduction of glycerol into the dispersion medium has caused polystyrene radicals to precipitate at a lower chain length, so producing a larger number of smaller nuclei compared with particles formed in methanol alone. The very narrow distributions of particle sizes displayed in *Figures 1* and *3* indicate that in these dispersion polymerizations, particle formation may be considered in terms of a nucleation–growth mechanism with no further nucleation during the progress of polymerization. Previous work[2–10] on the effect of alcoholic diluents on the size of polystyrene particles has been directed to particles in the size range of 1–10 μm. The results in *Figure 2* indicate that non-aqueous polar diluents are also effective for producing near-monodisperse particles in the sub-micrometre range.

Conclusions

It is demonstrated that partially hydrolysed poly(vinyl alcohol) (35 mol%) in methanolic media is effective as steric stabilizer in dispersion polymerizations of styrene as long as the stabilizer is present at a concentration to provide sufficient coverage of the surfaces of particles. Excess concentration of steric stabilizer above this minimum concentration produces little change in particle size. Near-monodisperse particle size distributions can be achieved and mean particle size in the range 0.5–3.0 μm can be controlled by varying the composition of the dispersion medium. Glycerol and ethanol were found to be codiluents in conjunction with methanol, with retention of the solubility of the partially hydrolysed poly(vinyl alcohol) in the dispersion medium. This initial communication has not addressed the anchoring and stabilizing mechanisms in relation to sequence length distributions of vinyl alcohol and vinyl acetate units, but it is suggested that such a study is relevant to producing particles with different surface characteristics by investigating a range of partially hydrolysed poly(vinyl alcohol) samples.

Acknowledgements

The authors thank John Cruden and Steve Ormondroyd for helpful discussions, Harlow Chemical Company Ltd for support, and John Bates and Frank Page for assistance with electron microscopy.

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