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SHORT COMMUNICATION

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Production of porous suspension polymers using a continuous tubular reactor

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Abstract The conventional method for the synthesis of porous cross-linked copolymer beads is by suspension polymerisation. Suspension polymerisation reactions are generally performed in a stirred tank, which generally results in a large size distribution. By careful control of the polymerisation conditions, polymer beads can be produced using a tubular poly(tetrafluoroethylene) continuous reactor. Such beads are produced with the same average pore size, but with a lower degree of polydispersity than analogous systems produced in a batch reactor (stirred tank). This is achieved by density-matching the droplet and continuous phases (by the use of a brominated monomer or a porogenic diluent) and increasing the viscosity of the monomer phase (with the addition of small amounts of polystyrene).

Key words Suspension polymerisation · Continuous tubular reactor · Porous beads

Introduction

Large beads, in the size range 1 μm to 1 mm, may be prepared by suspension polymerisation. In suspension polymerisation the initiator is soluble in the monomer phase, which is dispersed into the dispersion medium (usually water) to form droplets (i.e. an emulsion is formed). The presence of a droplet-stabilising agent (often a surface-active polymer) is usually required.

The stabilised monomer droplets may be considered as "microreactors", with the polymerisation proceeding therein [1–4]. This "mini–bulk" polymerisation is initiated thermally and allowed to proceed to completion [5]. The average size of the polymer beads formed is expected to be approximately the same as that of the initial monomer droplets. If the size distribution of the resultant polymer beads is broad, there may be some necessity for sieving to improve the size classification. Since sieving is an expensive, wasteful procedure, it is desirable to produce polymer beads with a narrow size distribution.

The polymer beads may be made porous by the inclusion of an inert diluent (or "porogen") to the monomer phase, which may be extracted after polymerisation [6].

During the early stages of a suspension polymerisation reaction, the size distribution of the polymerising droplets is dependent upon the balance between droplet breakup and droplet coalescence. For a stirred batch reactor this is controlled by the type and speed of agitator used, the volume fraction of the monomer phase, and the type and concentration of stabiliser used. It has been shown that in a batch reactor coalescence and droplet breakup occur in different regions of the reactor [7–10]. Coalescence is found to occur predominantly in the region of circulating flow (where the shear stress is not great), whereas droplet breakup is found to occur mainly in regions of high shear, such as in the vicinity of the agitator. The influence of turbulent flow in stirred tank reactors has been reviewed by Kresta and Wood [11, 12].

Chemical reactors used for polymerisation can in general be divided into three groups: batch, semicontinuous (comprising multistage stirred tanks) and continuous reactors. Batch reactors are widely used in industrial processes for the production of various polymers, in volumes up to the tonne scale. Batch reactors have the advantage of flexibility in terms of reactor operation for a relatively low capital investment. Drawbacks include inconsistent batch-to-batch quality and, should problems occur during reaction, the loss of an entire batch with the subsequent disposal problems.

Continuous polymerisation processes offer many advantages over reactions performed in batch. These include improved sample consistency, with reduced wastage when in-reactor variations occur. Continuous reactors can be divided into two types [2]: continuous tubular and Couette–Taylor flow reactors.

The concept of using a tubular continuous flow reactor for a thermally induced suspension polymerisation is attractive due to the low cost involved and the simplicity of the system, both in terms of construction and use. Implementation of such reactors on an industrial scale has been slow due to reservations regarding the properties of the product and concerns regarding operational problems, such as blocking. Tubular reactors can be divided into two types [3].

1. Loop reactors are those in which the production of the emulsion and the subsequent polymerisation are performed in the same vessel. These may consist of either a circular loop reactor [13, 14] or a loop reactor with an elbow [15]. Circulation for such a setup is achieved using a paddle-type stirrer positioned within the tube. For such a setup, the mechanism of droplet breakup has been studied [14, 15], and it has been shown that no coalescence or breakup of droplets occurs in the circulation region of the reactor. Furthermore, an increase in agitator speed or droplet stabiliser concentration results in a narrower droplet size distribution.
2. Two-step devices are those in which the emulsion is produced externally and then fed into a tubular reactor, in which the polymerisation reaction is performed [15]. The flow rates used are usually relatively low.

Whilst flowing through a tubular reactor of radius r, spherical emulsion droplets may experience some distortion into a prolate ellipsoid shape in the differing laminar flow field. This distortion will depend upon a balance between the interfacial tension forces and surface stresses from shear flow [16]. In order to disrupt a droplet of radius a, a pressure gradient ($\mathrm{d}p/\mathrm{d}r$) must be applied:

$$\mathrm{d}p/\mathrm{d}r \approx \Delta p/a = 2\gamma/a^2 \quad . \tag{1}$$

Δp is the Laplace pressure difference and γ is the interfacial tension. Laminar flow may be enough to produce such a gradient; however, droplet breakup will only occur for shear rates (D) where the dimensionless Weber number (We) (given by the following expression) becomes greater than 1:

$$We = Da\eta/\gamma > 1 \quad , \tag{2}$$

where η is the shear viscosity of the continuous phase [17]. In practice, the shear forces required to achieve such a breakup process are unlikely to be encountered in the tubular reactor.

The rate of droplet coalescence is controlled by liquid drainage between approaching droplets and more significantly by the rigidity of the two corresponding oil/water interfaces, since this controls the damping of thermally or mechanically induced oscillations in the film thickness. Adsorbed polymers help to increase the interfacial rigidity. An increase in the viscosity of the dispersed droplet phase may also impart increased stability to coalescence of the droplets by again increasing the rigidity of the droplet/water surface. Such an increase can be achieved by dissolving small amounts of the corresponding polymer in the monomeric phase. In the work described here, small amounts of polystyrene (◆ = 280,000) were dissolved in the dispersed (oil) phase (prior to emulsification).

As the polymerisation proceeds there will come a stage in the reaction where the partially polymerised beads become "sticky". Satellite droplets (formed by droplet breakup) may attach to the surface of the polymer bead. In a product designed for chromatographic columns, this will result in poor packing characteristics and brittle beads.

Experimental

Materials

The following chemicals were obtained from commercial sources: styrene, divinyl benzene (55%), (meta and para isomers), 2-ethylhexanoic acid, 2-bromohexanoic acid, 1-decanol, benzoyl peroxide (BPO) (70%), polystyrene (average = 280,000) and sodium chloride (Aldrich); glycidyl methacrylate (GMA) (Fluka); poly(vinyl alcohol) 88% hydrolysed ("Mowiol 40-88"; Hoechst) (PVA), 4-bromo styrene (96%) (Janssen Cimica). The monomers were purified by filtration through an aluminium oxide column to remove inhibitor. Deionised water (Purite) was used for making the aqueous phase. All purities were greater than 97% unless otherwise stated.

Viscosity measurements

Viscosity measurements were made on the monomer phase using a PSL ASTM-IP capillary viscometer placed in a thermostatted water bath at 25 °C (using toluene as a reference solution). Samples were left to equilibrate for a minimum of 2 h prior to measurement, and flow times were averages of at least five runs.

Emulsion stability

The stability of the monomer emulsion droplets was studied by performing lifetime measurements of a single droplet at the corresponding oil/water interface. The interface was created by placing a sample of aqueous dispersion into a glass vessel (to a height of 15 cm), then carefully placing the oil phase onto the surface (to a depth of 1 mm). A single droplet (with a volume of

0.005 ml) was produced at the bottom of the aqueous solution using an Agla syringe with a 26-gauge hypodermic needle (introduced through a Suba seal). Timing was started when the droplet touched the oil/water interface and was continued until the droplet was absorbed into the oil phase. Each measurement was an average of a minimum of ten experiments.

Preparation of the polymer beads

Emulsification was performed as a batch process in a glass 500 ml cylindrical round-bottomed flask. The continuous phase comprised 190.8 g aqueous solution of PVA (0.11% w/w) and sodium chloride (5.66% w/w). The aqueous phase was degassed, by heating to 70 °C to prevent air pockets forming in the continuous reactor, then allowed to cool. The dispersed organic phase comprised 15 g monomer, 15 g divinylbenzene (cross-linker), 24 g 2-ethylhexanoic acid (porogenic diluent), 0.35 g oil-soluble initiator (BPO) and 0.5 g polystyrene (0.93% w/w) (added to increase the viscosity of the oil phase).

Emulsification was achieved by shearing the organic and aqueous phases under an atmosphere of nitrogen for 1 h. Agitation was provided by a toothed-disc stirrer, rotating at 600 rpm with the stirrer blade kept at a constant distance of 1 cm from the bottom of the flask. The emulsion was then placed into a gently stirred holding tank, from which it was introduced into the reactor.

The continuous reactor consisted of a coiled poly(tetrafluoroethylene) (PTFE) tube (Teflon) of internal diameter 7.9 mm and wall thickness 0.8 mm. Prior to the introduction of the emulsion, the tube was flushed through with the continuous phase. The emulsion was fed through the reactor at a flow rate of 180 ml h^{-1}, using a Fluid Metering QG6 pump at the far end of the tube. This type of pump is operated by a valveless positive displacement, which provides a relatively smooth flow without subjecting the solution in the pump head to large stresses. A solution of sodium chloride in water (5.66% w/w) was flowed through the reactor after the emulsion.

Polymerisation was performed at 70 °C by placing the continuous reactor in a thermostatted water bath. The solution was fed through the reactor using a pump at the far end of the tube such that the polymer beads, rather than the more fragile emulsion droplets, passed through the pump. The residence time used was dependent upon the monomer system used [18], but was sufficient to allow polymerisation to proceed to completion, plus an additional hour. Residence times were varied by the use of differing lengths of PTFE tubing, which, in general, was greater than 20 m in length.

For batch polymerisation reactions, emulsification and polymerisation were performed in the same glass reactor. Emulsification was achieved in an identical manner to emulsions produced for the continuous reactor. The agitator speed was reduced to 400 rpm during polymerisation, which was performed at 70 °C using a thermostatted water bath. Polymerisation was allowed to proceed to completion overnight.

The resulting polymer beads from both the continuous and batch reactors were washed, sequentially, with water, aqueous sodium hydroxide solution (1.0 M), ethanol and acetone. This procedure removes the porogenic diluent and any unreacted monomer. The beads were then dried under vacuum.

Characterisation of the copolymer beads

The size distribution of the beads was determined using a ‘Malvern’ Mastersizer MS1000. The beads were then fractionated using a 300-μm stainless-steel sieve to yield two fractions. The pore size distribution, pore volume and surface area of the larger size fraction were investigated by mercury porosimetry, using a ‘Quanta Chrome’ Autoscan 60 porosimeter, operating in the range 0–380 MPa.

Results and discussion

The viscosity of the oil phase, comprising styrene (27.8% w/w), divinylbenzene (27.8% w/w) and 2-ethylhexanoic acid (44.4% w/w), as a function of added polystyrene is shown in Fig. 1. The molecular weights of the polystyrene samples used were approximately 100,000, 280,000 and 560,000. As a comparison, the viscosity of an oil sample comprising GMA (27.8% w/w), divinylbenzene (27.8% w/w) and 2-ethylhexanoic acid (44.4% w/w) without polystyrene present was also determined. As expected the addition of a relatively small amount of polystyrene results in a substantial increase in the viscosity of the oil phase. The molecular weight of the polystyrene added also has an effect on the magnitude of the viscosity increase. The viscosity of the oil phase produced with GMA (with no polystyrene added) is greater than that obtained for styrene.

The effect on droplet stability of the addition of polystyrene (≈280,000) to the oil phase was also studied, by measurement of the lifetime of a droplet (of fixed size) at the oil/water interface (containing polymeric stabiliser and salt) and is shown in Fig. 2. The oil phase comprised styrene (27.8% w/w), divinylbenzene (27.8% w/w) and 2-ethylhexanoic acid (44.4% w/w). Droplets formed in the absence of polymeric stabiliser were absorbed immediately into the oil phase. The presence of PVA was found to increase the lifetime of the oil droplet at the interface to more than 1 min. The addition of small amounts of polystyrene was found to increase the stability, resulting in droplet lifetimes of greater than 5 min.

For polymers produced in the continuous reactor, the preformed emulsion was placed into a gently stirred holding tank, from which it was introduced into the PTFE tubular reactor. Initial experiments were per-

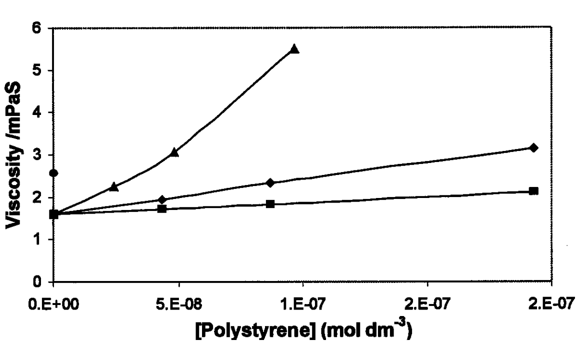

Fig. 1 Viscosity of dispersed (oil) phase determined by capillary viscometry as a function of added polystyrene concentration. For styrene/divinylbenzene/2-ethylhexanoic acid systems, three molecular weights of polystyrene were studied: (■) ≈ 100,000, (◆) ≈ 280,000 and (▲) ≈ 560,000. The viscosity of a glycidyl methacrylate/divinyl benzene/2-ethylhexanoic acid system (without polystyrene) is also given for comparison (●)

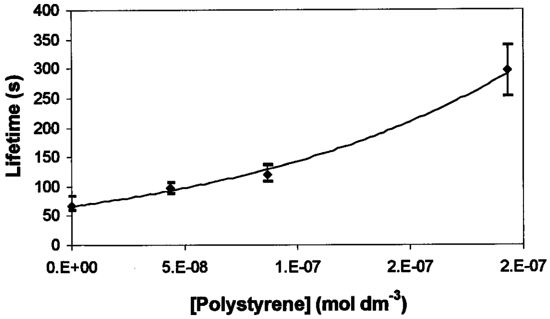

Fig. 2 Lifetime of a single oil droplet (of approximate diameter 2.1 mm) at the oil/water, containing poly(vinyl alcohol) and NaCl, interface as a function of added polystyrene (◆ ≈ 280,000)

formed using a stainless-steel reactor, which was found to be prone to fouling. This may be attributed to

1. The surface energy of the steel. The wetting properties of the steel surface may be unsuitable encouraging particle–surface coalescence.
2. Ion contamination. The quality of the steel (e.g. at the welds) may be insufficient to eliminate electrochemical dissolution of ions (e.g. Fe^{3+}).

These problems were overcome by changing the reactor material to PTFE. The use of PTFE has various advantages over steel, including the absence of ions to dissolve in the emulsion, flexibility and a low surface energy.

Initial polymerisation runs using the PTFE continuous reactor highlighted an additional form of droplet instability, namely creaming of the droplet phase against the upper wall of the tube. This is caused due to density differences between the droplet phase and the dispersion medium. This problem was overcome by density-matching the two component phases, by increasing the density of the droplet phase: this was achieved using brominated species. Two recipes were used: one using a denser monomer (4-bromostyrene) and the other using a denser porogenic diluent (bromohexanoic acid). Using such modified recipes it was possible to produce porous polymer beads without fouling of the reactor occurring. For both recipes, density-matching of the droplet and continuous phases were achieved. The system with denser monomer (recipe A) comprised 7.5 g GMA, 7.5 g 4-bromostyrene, 15 g divinylbenzene, 24 g 4-methyl-2-pentanol and 0.5 g polystyrene. The system containing a denser porogenic diluent (recipe B) comprised 15 g GMA, 15 g divinylbenzene, 13 g 2-bromohexanoic acid, 11 g 1-decanol and 0.5 g polystyrene. The use of a monomer with increased density (bromostyrene, $\rho = 1400$ kg m^{-3}) as part of recipe A resulted in the successful production of polymer beads, using the continuous reactor. However, a denser porogenic diluent in the form of 2-bromohexanoic acid ($\rho = 1370$ kg m^{-3}) (recipe B) may potentially be recovered after polymerisation and reused. An additional benefit of this recipe is that it allows the use of more standard (cheaper) monomers.

For each of the polymerisations performed in the continuous reactor, a similar reaction was performed as a batch reaction. This allows the determination of the effects of the polymerisation method on the particle size distribution and the average pore size of the beads produced. The bead size distributions obtained are shown in Fig. 3 for recipe A and in Fig. 4 for recipe B. From the data shown in Figs. 3 and 4, the size distribution for the sample produced using the continuous tubular reactor is much narrower than that obtained by the batch reaction.

The pore size distribution (for the bead fraction having a diameter greater than 300 μm) was determined for both recipes using mercury porosimetry. The data for recipe A are plotted as d*V*/d(log *P*) against pore radius (where *V* is the volume of mercury which has penetrated and *P* is the pressure) in Fig. 5. Average pore sizes, for recipes A and B (produced both as a batch and in the continuous reactor) are given in Table 1. From the data in Fig. 5 and in Table 1, it is apparent that the type of reactor employed (continuous or batch) in the production of polymer beads appears to have little effect

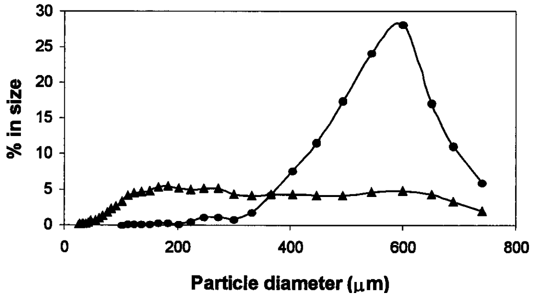

Fig. 3 Average particle diameter of beads prepared using recipe A (denser monomer) determined using a Malvern Mastersizer: sample produced in a batch (▲) and sample produced using the tubular continuous reactor (●)

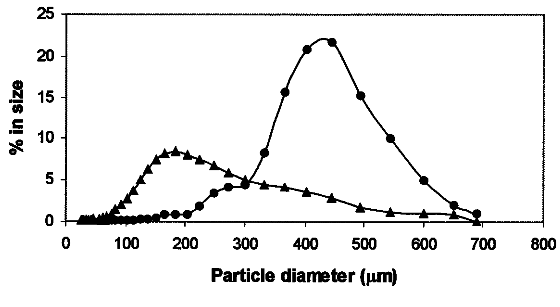

Fig. 4 Average particle diameter of beads prepared using recipe B (denser porogenic diluent) determined using a Malvern Mastersizer: sample produced in a batch (▲) and sample produced using the tubular continuous reactor (●)

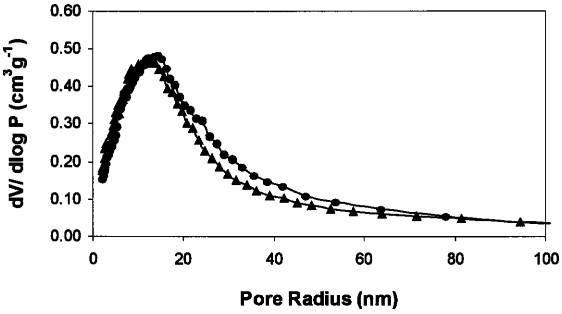

Fig. 5 Pore size distribution (for fractions greater than 300 μm) determined by mercury porosimetry. d*V*/d(log *P*) versus pore radius for beads prepared using recipe A (denser monomer): sample produced in a batch (▲) and sample produced using the tubular continuous reactor (●)

Table 1 Average particle diameter of beads prepared determined using a Malvern Mastersizer and average pore sizes (for fractions greater than 300 μm) determined by mercury porosimetry

Recipe	Reactor type	Average diameter (μm) span[a] (in parentheses)	Average pore radius (nm)
A	Batch	399 (2.21)	19.7
A	Continuous	569 (0.56)	20.3
B	Batch	204 (1.37)	31.0
B	Continuous	381 (0.55)	32.4

[a] Span is the manufacturer's quoted measure of polydispersity for the Malvern Mastersizer and may be defined as

$$\text{Span} = \frac{D(v,0.9) - D(v,0.1)}{D(v,0.5)} ,$$

where $D(v,p)$ is the volume-averaged diameter at the percentage point shown. This gives a measure of the width of the volume distribution relative to the median diameter, $D(v,0.5)$

on the average pore size obtained. The average pore size obtained is, however, dependent upon the type of porogenic diluent used and the composition of the monomer phase.

The broadening of the particle size distribution in a batch reactor is mainly a result of nonuniform circulation of the droplets between the high-shear and low-shear regions, which can result in the breakup of droplets [19, 20]. In the continuous reactor used in this work, the turbulence experienced by the emulsion droplets is more uniform by distribution, which results in the majority of droplets experiencing the same conditions of droplet coalescence and breakup [15]. Only droplets at the wall of the reactor will experience significant shear forces, which will result in a reduction in the rate of droplet breakup compared with the same reaction performed in a stirred tank (batch).

Park and Blair [21] studied the flow of emulsion droplets through a tubular reactor driven by an impeller at one end of the reactor. They concluded that in a tubular reactor droplet breakage is virtually nonexistent (even at relatively short distances from the impeller). Tanaka and O'Shima [15] used a similar approach to study the average emulsion droplet size throughout the length of a tubular reactor. They concluded that since the particle size remained unchanged droplets flowing through a tubular reactor experience no significant coalescence.

Tanaka and O'Shima studied the deposition of polymer on the walls of a continuous reactor and found that the amount deposited decreases with increasing Reynolds number. For a tubular reactor of diameter *D*, the Reynolds number *Re* may be defined as

$$Re = \frac{\rho U D}{\mu} , \tag{3}$$

where ρ is the density and μ the kinematic viscosity of the continuous phase and *U* is mean flow velocity. Under the normal operating conditions of a continuous reactor, the Reynolds number is so high that deposition of polymer on the reactor walls should not occur [15]. Conversely, for a stirred tank reactor, an increase in the coating of the reactor walls with polymer is observed with increasing Reynolds number [22].

For reactions performed in the continuous reactor the size distribution of the beads formed is limited by the size distribution of the original emulsion. In the work described, emulsification was performed by shearing the component phases. This results in a distribution of emulsion droplet sizes. The size distribution of the beads produced using the continuous reactor may be further reduced by the use of more "nonstandard" polymerisation devices, such as rotating disks [23–25], rotating cylinders [26, 27], vibrating nozzles [28, 29] and cross-flow membranes [30].

Conclusions

For PVA-stabilised oil-in-water emulsion droplets, the addition of relatively small amounts of polystyrene to the oil phase results in an increase in the viscosity of the droplets. This has a stabilising effect upon the droplets by reducing drainage from between droplets; this can help reduce droplet breakup during polymerisation.

By the use of bromine-containing species (either in the form of brominated monomers or porogenic diluents), it is possible to match the densities of the dispersed and continuous phases. This will reduce the propensity for droplet creaming to occur. Using such a recipe (with polystyrene added for additional stabilisation) it is possible to produce large porous cross-linked polymer beads by suspension polymerisation using a PTFE tubular reactor without blocking of the reactor occurring. The size distributions of beads produced using a tubular reactor show significant improvement over those for similar beads produced as a batch reaction, without any significant effect on the average pore size obtained.

Suspension polymerisation reactions using the continuous tubular reactor described should, in principle, be possible with other monomer systems (e.g. styrene) with the appropriate residence times and modifications to recipe B. This would involve variations in the ratio of the two porogenic diluents used, such that density of the droplet and continuous phases are matched.

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