Monodisperse Polymeric Particles by Photoinitiated Precipitation Polymerization

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ABSTRACT: Monodisperse polymer particles consisting of DVB and styrene-*copoly*-DVB were successfully synthesized by photoinitiated precipitation polymerization with 2,2′-azobis(2-methylpropionitrile) (AIBN) as initiator. A focused 150 W xenon short arc lamp was used to radiate the sample mixtures. The size of the particles ranged from 1.5 to 4 μm and could be varied by changing the monomer concentration between 2 and 10% (v/v) and by means of the time of polymerization. By using photoinitiation instead of thermal initiation, it was possible to avoid coagulum and arrive at spherical particles with an exceptionally high monodispersity for particles of this size range (polydispersity index < 1.02) and with monomer loadings well above 5%.

Introduction

Nonporous monodisperse micrometer-sized particles have been used as packing materials in liquid chromatography for the past decades,[1,2] and the interest concerning particles of these dimensions has recently been augmented by the commercial focus on ultrahigh-pressure liquid chromatography. The attractive features of nonporous micron-sized particles are that they are not restricted by diffusion limitation in the stagnant mobile phase.[3] They are therefore well suited for separation of both large and small molecules, either underivatized or after grafting of functional groups on the surface.[4,5] Highly cross-linked polymeric particles consisting of divinylbenzene (DVB) and styrene-*copoly*-DVB (St-DVB) can be used at any aqueous pH, withstand high pressure, and are also heat-resistant.[6−9] Because of these chemical and physical properties, they may serve as an alternative to more traditional chromatographic separation materials such as silica, which is limited in its applicable pH range. Particles of narrow particle size distribution based on styrene and DVB have been made by dispersion polymerization, often with poly(*N*-vinylpyrrolidinone) as steric stabilizer to produce micron-sized particles in a single batch.[10−12] These polymerizations have been carried out in numerous solvents where methanol and ethanol have been most common.[4,12] Dispersion polymerization needs precise optimization to achieve a reasonably narrow disperse size distribution, especially when there is a high degree of cross-linking.[13] Recently, Winnik's group presented a way to make cross-linked polystyrene particles of narrow polydispersity by a two-stage dispersion polymerization, where DVB or ethylene glycol dimethacrylate (EGDMA) was added as cross-linker after the nucleation stage.[14] However, the amount of cross-linker used was only 1 wt %.

In 1993, Stöver's group first reported the preparation of spherical monodisperse DVB particles by precipitation polymerization using thermal initiation.[6] Among several other solvents with solubility parameters (δ) in the range 9.1−14.5, acetonitrile ($\delta = 12.1$) was chosen because it was found to be a near-Θ solvent for the polymer, which eliminates the need for steric stabilizers. The monomer and initiator are also soluble in the solvent, and they form a homogeneous mixture. As the polymer forms, it becomes insoluble in the solvent and precipitates as a result of this to form a milky suspension. Because of the high amount of cross-linking, the growing particles are self-stabilized with a clean and rigid surface.[13] Since the monomer contributes to the overall solvent properties, in particular during the early stages of polymerization, monomer loading must be kept relatively low (typically 2−5%) in precipitation polymerization compared to dispersion polymerization, where concentrations up to 40 vol % are common.[4,6,15] Bai et al.[16] have used what they called a "distillation precipitation polymerization" and managed to get coagulum-free microspheres of DVB-80 with a monomer loading of 7.5% (v/v) when acetonitrile was continuously distilled off from the reaction vessel (a flask attached to a rotary evaporator) to maintain a high monomer concentration throughout the polymerization. Precipitation polymerization has not only been applied for homopolymers with cross-linking ability (e.g., DVB) but also for copolymers. For instance, styrene,[7,8] maleic anhydride,[17] and different methacrylates[18,19] have been copolymerized with DVB to form monodisperse microspheres. Choe and co-workers recently accomplished the copolymerization of styrene[8] and methyl methacrylate (MMA)[19] with 50% DVB at total monomer loadings of up to 15 vol %. Coagulum-free microspheres were produced with both styrene and MMA as comonomers, although with a relatively high polydispersity and evidence of excessive particle coalescence at higher monomer loadings.[8]

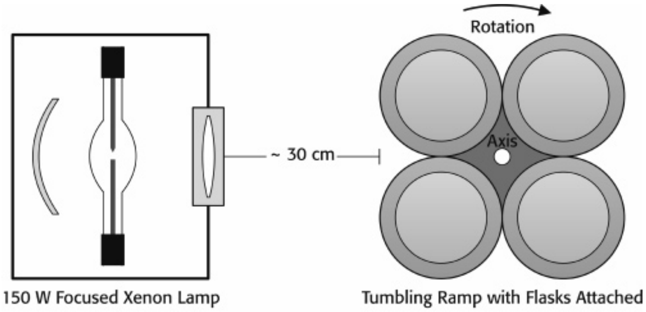

Figure 1. Schematic drawing of the photopolymerization setup with the four 250 mL polymerization flasks mounted on a bracket rotating around an axis. The four flasks were rotating at 5−15 min^{-1} and were in the directly irradiated beam of the focused Xe lamp approximately one-fourth of the total polymerization time.

Gentle agitation is generally required in precipitation polymerization and is typically accomplished by slowly rotating, shaking, or rocking the reaction vessel.[6−8,13,14] Preparation of

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Table 1. Particle Size and Yield at Varying Monomer Loading for DVB and St-DVB Particles

					D_n[b] (μm)		CV[c] (%)			
sample id	DVB (vol %)	St-DVB (vol %)	AIBN (wt %)	time[a] (h)	SEM	SLS	SEM	SLS	U[d]	yield[e] (%)
05-1-045	6		2	163	3.91	3.92	3.0	5.2	1.002	27.6
05-1-046	4		2	163	3.10	3.13	4.0	6.4	1.004	26.0
05-2-043		4	2	163	3.74	3.91	8.2	5.9	1.017	23.1
05-2-044		2	2	163	2.70	2.70	8.5	5.2	1.015	17.2

[a] Polymerization time. [b] Number-average particle size. [c] Coefficient of variation. [d] Polydispersity index. [e] Expressed as weight of recovered particles in percent of monomer loaded.

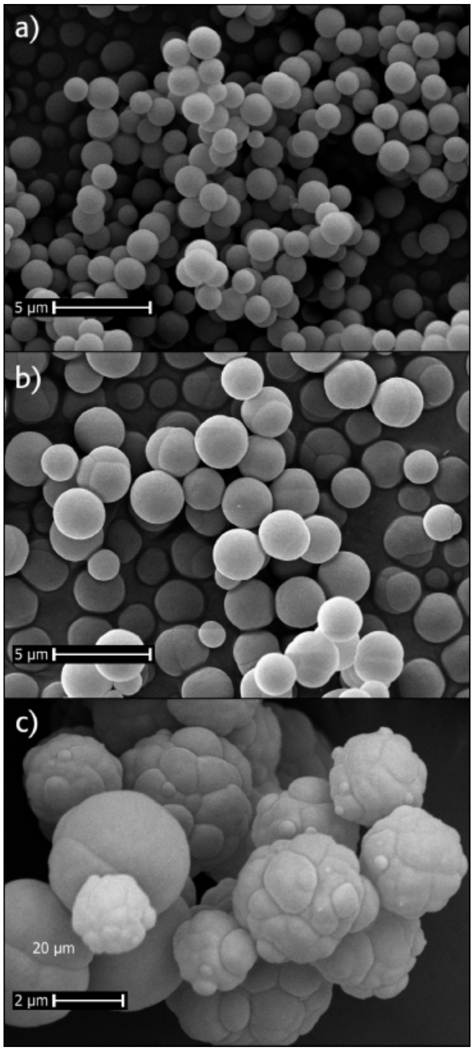

Figure 2. Results from initial attempts using thermally initiated precipitation polymerization. Micrographs (a) and (b) show DVB particles that are either polydisperse or where several particles are coalesced, whereas (c) shows St-DVB particles where the amount of cross-linker was lower.

microspheres by precipitation polymerization has almost invariably taken place by thermally induced free radical initiation, triggered by conducting the polymerization in a water bath or in a circulating air compartment at 60−70 °C. One exception is polymerization induced by ionizing radiation that produces polymeric particles in a single batch from a monomer solution consisting of various acrylic and methacrylic monomers with oligo(ethylene glycol) dimethacrylate as cross-linkers, without the use of dedicated initiators. The monomer solution is mixed with organic solvent and irradiated with γ-rays from a ^{60}Co source, and no stabilizers or surfactants are needed.[20−22]

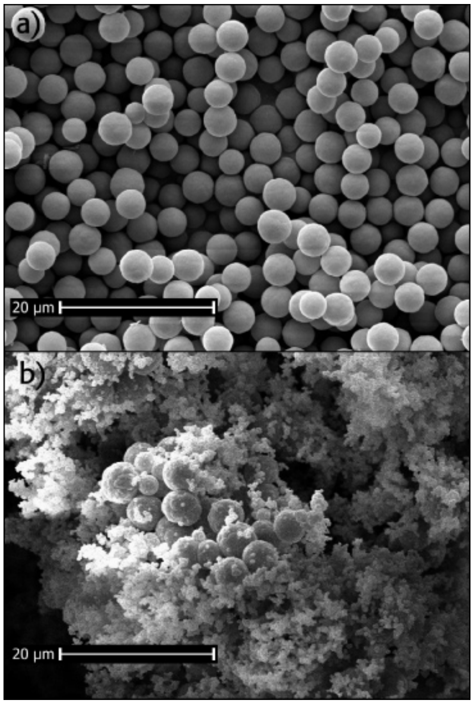

Figure 3. SEM micrographs for (a) DVB and (b) St-DVB polymerizations at 10% (v/v) monomer loadings.

Thermally initiated precipitation polymerization is currently a well-established method for producing monodisperse microspheres in the range 1−5 μm, and much effort has been focused on getting better control over the polymerization process. Important parameters such as the choice of solvent and cosolvents and the concentrations of monomer and initiator have been investigated and shown to play a crucial role for arriving at the right size and morphology. The interplay between these parameters is particularly important, since the particles are self-stabilized. Because of the use of thermal initation, experiments with varied temperature are compounded by the initiator decomposition rate, and the effect of temperature on stability cannot be studied separately. We were therefore curious to investigate the preparation of microparticles by photoinitiated precipitation polymerization, since these experiments can be carried out at lower temperature.[23] Reported here is a novel single-step photoinitiated precipitation polymerization procedure for producing nonporous DVB and St-DVB particles, using UV-initiated cleavage of the azo initiator AIBN, which is the most common initiator in thermal precipitation polymerization recipes. Particle properties such as average particle diameter, surface area, and pore size distribution were investigated.

Experimental Section

Chemicals. Divinylbenzene (DVB-80, technical grade) consisting of 80% divinylbenzene isomers (Fluka, Buchs, Switzerland) and styrene (Acros Organics, Geel, Belgium) were freed of inhibitors by passing them through basic Al_2O_3 (Aldrich, Milwaukee, WI). Initiator 2,2′-azobis(2-methylpropionitrile) (AIBN; Serva, Heidel-

Table 2. Particle Size and Yield with Increasing Initiator Concentration[a]

				D_n (μm)		CV (%)				
sample id	DVB (vol %)	AIBN (wt %)	time (h)	SEM	SLS	SEM	SLS	U	surface area (m^2/g)	yield (%)
05-1-035	4	2	88	1.72	1.74	7.4	6.8	1.014	108.9	15.5
05-1-036	4	2	112	2.31	2.37	5.4	6.7	1.008	77.8	18.9
05-1-037	4	4	88	2.28	2.31	5.0	8.1	1.007	77.7	19.5
05-1-038	4	4	112	2.58	2.75	7.9	5.8	1.016	75.7	22.9

[a] See Table 1 for an explanation of the headings.

Table 3. Replicates of DVB and St-DVB Particles Showing Reproducibility for the Experiments[a]

					D_n (μm)		CV (%)				
sample id	DVB (vol %)	St-DVB (vol %)	AIBN (wt %)	time (h)	SEM	SLS	SEM	SLS	U	surface area (m^2/g)	yield (%)
05-1-031	3		2	52	1.46	1.46	5.6	7.9	1.008	73.5	10.1
05-1-033	3		2	52	1.52	1.55	4.8	8.9	1.006	74.0	N/A
05-1-034	3		2	52	1.57	1.58	7.2	8.1	1.012	73.0	N/A
05-2-043		4	2	163	3.74	3.91	8.2	5.9	1.017	5.5	23.1
05-2-047		4	2	163	3.69	3.65	7.3	6.0	1.014	5.2	22.7
05-2-044		2	2	163	2.70	2.70	8.5	5.2	1.015	5.2	17.2
05-2-048		2	2	163	2.92	3.13	9.0	6.6	1.022	5.5	17.3

[a] See Table 1 for an explanation of the headings.

berg, Germany) was used as received. Acetonitrile, analytical grade (Fischer Scientific, Loughborough, UK), was used as solvent and dried with 3 Å molecular sieves before use. Organic solvents such as acetone (Fischer Scientific), ethanol (99.5%; Solveco Chemicals AB, Täby, Sweden), methanol, and tetrahydrofuran (J.T. Baker, Deventer, Holland) were of analytical grade and used without further purification.

Polymerization. The polymerizations were carried out in 250 mL polypropylene (in some cases Teflon PFA) flasks from Nalge Nunc (Rochester, NY), and the monomer content was varied between 2 and 10% (v/v) with respect to the acetonitrile solvent. The AIBN initiator (2% w/w or in some cases 4% w/w with respect to the monomer concentration) was added, and the flasks were shaken until all initiator was dissolved. Before the polymerization was initiated the solution was degassed for at least 5 min by nitrogen purging to remove dissolved oxygen. The flasks were attached four at the time to a custom-made rotation device and tumbled around a central axis by means of a geared-down dc motor at speeds varying between 5 and 15 min^{-1}. A 150 W short arc xenon lamp with focusing optics was directed from the side toward the center of the flask cluster at a distance of 30 cm. This type of lamp has a continuous spectrum that spans from deep ultraviolet to infrared, and the light was not filtered. The chosen initiator AIBN decomposes at wavelengths (300−400 nm) where the UV absorption of styrene and divinylbenzene in acetonitrile does not overlap. The lamp was only irradiating on one flask at the time, but the rotation brought each flask into the intense light path every 4−12 s. In reality, this means that the true radiation time was only about one-fourth of the total time. For a schematic representation of the polymerization setup, see Figure 1. The reaction time was varied from 24 to 163 h, and during operation the heat caused by the lamp increased the temperature in the reaction flasks from room temperature to about 31 °C. For particles consisting of both styrene and DVB the molar ratio was fixed at 1:1. After polymerization the solvent and unreacted monomer were filtered off by suction filtration using 0.45 μm nylon membrane filters (Millipore, Bedford, MA) or in some cases a G5 sintered glass filter. The particles were resuspended in acetone and placed on a shaker for 2 h. This procedure was repeated with ethanol, and the particles were then washed three times with tetrahydrofuran and finally dried in a vacuum oven at 40 °C at ~2 kPa pressure for 24 h.

Characterization. The size and morphology of the particles were characterized by scanning electron microscopy (SEM) using a Cambridge 360ixp microscope run with a LaB$_6$ electron emitter (Leica Cambridge Ltd, Cambridge, UK). Micrographs were recorded in randomly selected particle populations and areas at different standardized magnifications, and all specimens were prepared according to standardized methods. Samples were attached to sticky carbon tape mounted on alumina stubs (Agar Scientific Ltd, Stanstead, UK) and thereafter evaporation-coated with ~15 nm of carbon and gold in an Edwards E12 vacuum coating unit (Edwards High Vacuum Ltd., Crawley, UK). From each of the SEM micrographs 100 particles were measured. Prior to the measurement the image was divided into four identically sized parts, and the particles were counted from the upper left corner and proceeding horizontally across then with the next "row" until 25 particles with identifiable diameter had been measured in each quarter image. In some samples, up to 1000 particles were counted to check the convergence of the polydispersity index. For those samples, it was clear that the value converged to less than 5% error after 250−500 counted particles and that a lower count gave a slightly high value. The combined diameters were used to calculate the number-average diameter D_n and the weight-average diameter D_w using the following equations:[9,24]

$$D_n = \frac{\sum N_i D_i}{\sum N_i} \tag{1}$$

$$D_w = \frac{\sum N_i D_i^4}{\sum N_i D_i^3} \tag{2}$$

N_i is the number of particles measured, and D_i is the diameter of the measured particle. By using D_n and D_w, the polydispersity index U was calculated. The particle distribution is considered to be monodisperse when the polydispersity index is between 1.0 and 1.1.[24]

$$U = \frac{D_w}{D_n} \tag{3}$$

The manual particle counting from SEM images was complemented by static laser scattering measurements (SLS) using a Saturn DigiSizer 5200 (Micromeritics, Norcross, GA). The samples were dispersed in ethanol and first manually sonicated prior to the measurement and then additionally for 30 s in the DigiSizer recirculation loop (ethanol as recirculation liquid) to minimize particle aggregation. The SLS measurements were based on number frequency statistics and yielded a coefficient of variation.

A Micrometrics Tristar 3000 automated gas adsorption analyzer was used to measure the multipoint surface area and average pore

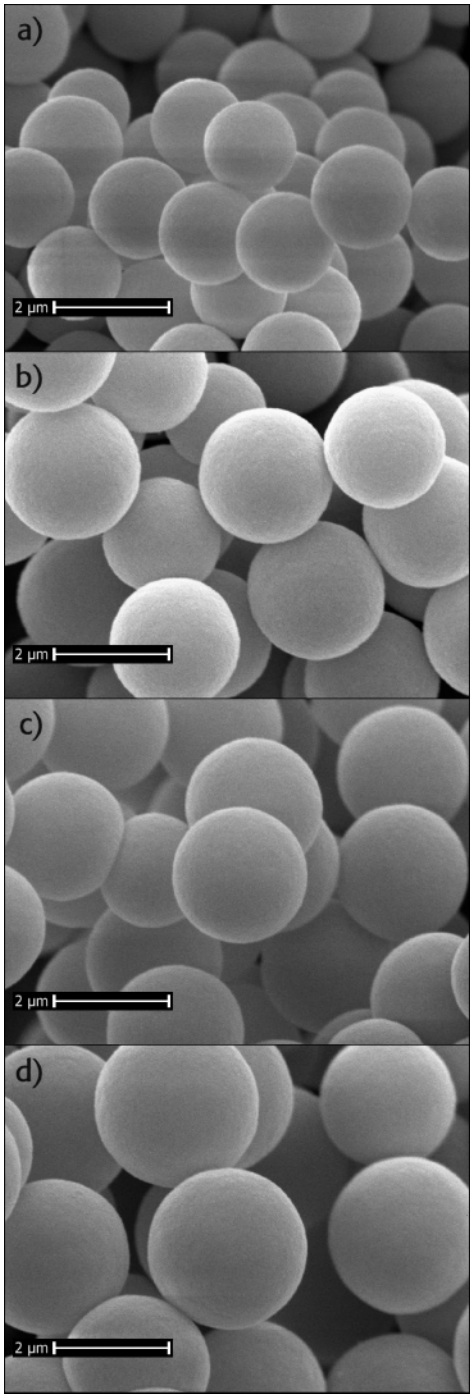

Figure 4. SEM micrographs of DVB particles recorded at 15 000 times magnification where (a) and (b) have an initiator concentration of 2 wt %. The particle size increased from 1.72 to 2.31 μm when the polymerization time increased from 88 to 112 h. Particles in micrograph (c) were prepared with 4 wt % initiator at 88 h reaction time, yielding practically the same particle size (2.28 μm). Micrograph (d) is the same system as in (c) but reacted for 112 h, showing further growth of the particles with maintained monodispersity.

width of the particles based on the Brunauer−Emmett−Teller equation.[25] The Tristar 3000 was also used to calculate the total pore volume of the particles by measuring N_2 adsorption close to atmospheric pressure. Before analysis the particles were dried in a vacuum oven at 40 °C overnight to remove adsorbed gases from the pores. Approximately 100 mg of particles was placed in a sample tube and dried again before analysis at 120 °C for at least 3 h under a continuous nitrogen flow, using a Micrometrics SmartPrep degassing unit.

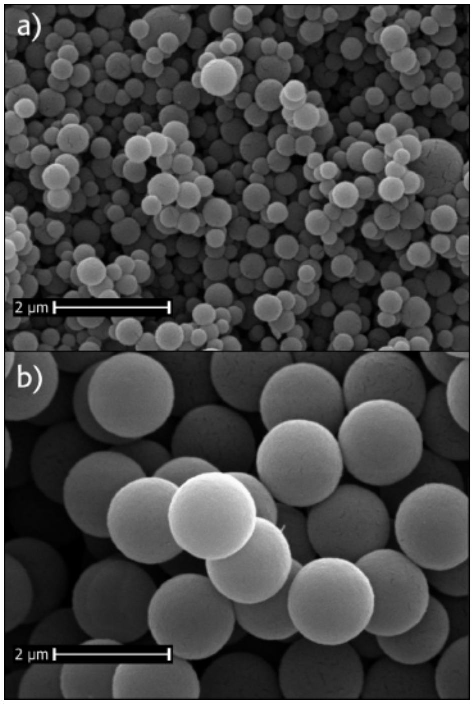

Figure 5. SEM micrographs showing size growth and a concomitant substantial decrease in polydispersity index of DVB particles: (a) after 24 h, $U = 1.52$; (b) after 64 h of polymerization, $U = 1.016$. Magnification of 15 000.

Results and Discussion

Our interest in highly monodisperse and cross-linked micron-sized particles stems from their utility in liquid chromatography. We were especially searching for particles with residual vinylic groups on the surface, since these are amenable to further reactions by various grafting schemes. Our initial approach was to use thermally initiated precipitation polymerization according to the procedures developed by Stöver et al.[6,14] However, when the reaction flasks were submerged in a water bath at elevated temperature, we experienced monomer mixture leaking out into the water bath due to the pressure created in the polypropylene flasks by N_2(g) released as a byproduct by the initiator, coupled with the vapor pressure of acetonitrile. During the initial polymerizations we also noticed substantial amounts of coagulum and polydisperse particles (Figure 2). Since we have previously used photoinitiation successfully for the preparation of separation materials[26] and acetonitrile is transparent to the UV-C radiation used in photoinitiation, we decided to investigate a photoinitiated precipitation polymerization scheme. Another reason for testing an alternative approach was the high sensitivity of thermally initiated precipitation polymerization to small changes in the setup, so photoinitiation by rotating the reaction vessels in air without heating seemed to be an interesting alternative. The initial results were encouraging but the polymerization appeared to be slow. We therefore decided to investigate a broader set of parameters that are known to influence the thermal variant, including monomer composition and concentration, initiator concentration, temperature, rotation speed, and time of polymerization.

Monomer and Initiator Concentrations. In thermally initiated precipitation polymerization, particle diameter and yield are known to increase with higher monomer loading.[6,8,16,19] Our results for the photoinitiated polymerization are shown in Table 1 and correspond to previous published results with respect to increase in size and yield. The highest monomer concentration tested was 10% (v/v). At that monomer loading spherical

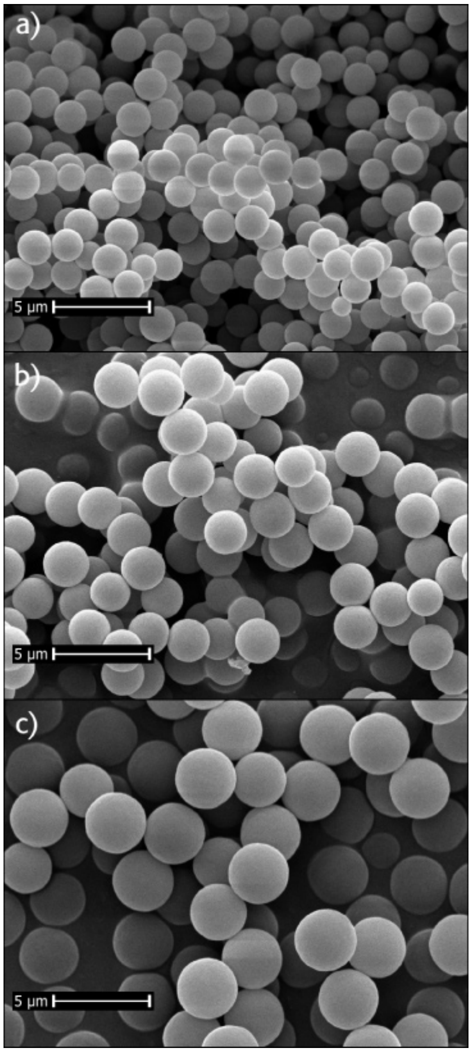

Figure 6. SEM micrographs of DVB particles polymerized using 4% (v/v) DVB monomer and 2 wt % AIBN initiator varying the time of polymerization from (a) 88 h, (b) 112 h, to (c) 163 h. Magnification on the three micrographs above is 5000.

monodisperse particles were still produced without any coagulum when DVB was used alone (Figure 3a). With St-DVB, particles were still achieved at 10% (v/v) monomer loading, but they had cauliflower shapes and were mixed with a coagulum (Figure 3b). With monomer concentrations 8% (v/v) and above, there was a tendency of particles to stick to the walls on the polypropylene flasks. These particles adhering to the wall could easily be wiped off the wall after the polymerization was finished, but it appeared that their separation from the bulk solution during polymerization caused an inhomogeneous particle buildup since a somewhat broader particle size distribution was seen in those experiments.

Experiments were also carried out where the initiator concentration was changed from 2 to 4% (w/w), with the monomer concentrations fixed at 4% (v/v). Similar to thermally initiated polymerizations, an increased particle diameter was seen as a result of the increased initiator concentration (Table 2). A doubled initiator concentration gave particles with practically the same size, monodispersity, surface area, and yield as an increase in polymerization time from 88 to 112 h at the lower initiator concentration level. The particles resulting from these experiments are shown in the micrographs in Figure 4. Since both the yield and size of the particles were the same for the two experiments, 2% (w/w) initiator was considered to be sufficient and used for the rest of the experiments.

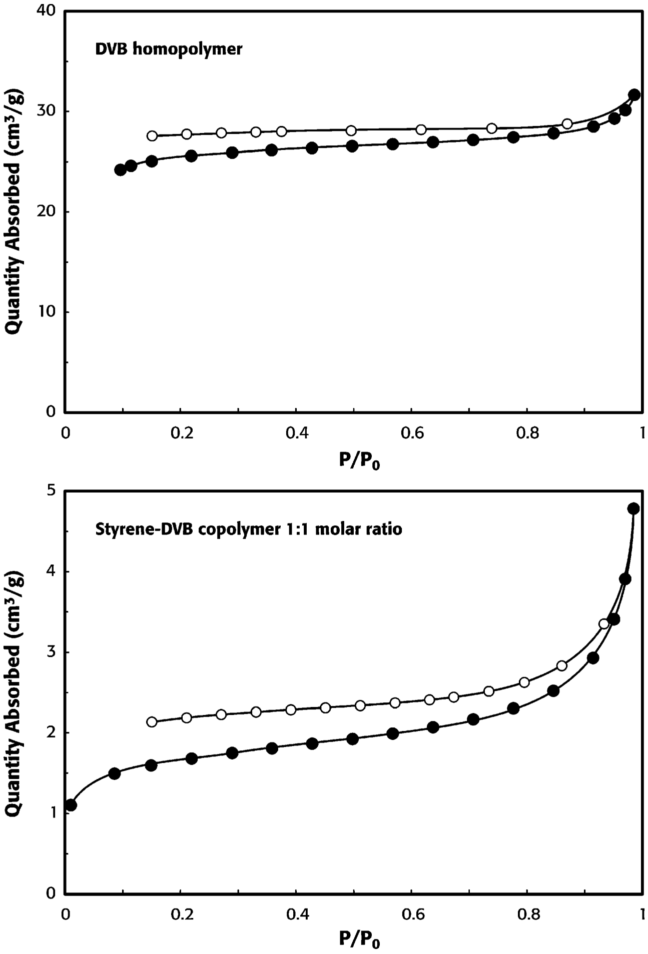

Figure 7. Nitrogen sorption (●) and desorption (○) curves for DVB homopolymer and St-DVB copolymer particles photopolymerized in acetonitrile for 163 h with 4% (v/v) monomer loading and 2% (w/w) AIBN initiator with respect to the monomer.

Particle Formation. In general, the particle formation is much slower when photoinitiation close to room temperature is used. In thermal initiation, the solution turns turbid in less than 1 h while photoinitiation takes several hours to reach this stage, depending on the monomer concentration. For thermal initiated precipitation polymerization the monomer conversion is high in the beginning and then levels off to reach a plateau after 24 h of polymerization.[13] With photoinitiation on the other side, a plateau was never reached in the monomer conversion within the 1 week time frame of the experiment. As mentioned above, increases in both initiator and monomer concentrations sped up the polymerization, leading to faster particle growth, (e.g., conversion rate), but at the same time the risk of coagulum increased due to interactions between the particles. Thermal initiation has been reported to result in coagulum at monomer concentration above 5% (v/v).[6] With photoinitiation we obtained coagulum-free spherical particles with monomer loadings as high as 10% (v/v) for DVB particles, whereas 8% (v/v) was the highest monomer concentration that gave spherical monodisperse particles with St-DVB. According to Downey et al.,[13] the stabilization mechanism involves capture of oligomers that form a solvent-swollen surface gel layer, which subsequently cross-links and builds the solid particle. The high monodispersity, the smooth surface, and the absence of coalesced particles evident in the particles produced by slow photopolymerization

(Figure 4) could be the result of more time being allowed for the captured oligomers to cross-link, which should result in a thinner gel layer on the particle surface. This may in turn affect the ability to capture oligomers from solution, but it also seems to effectively prevent particle interactions that could lead to coagulum formation or cauliflower-shaped coalesced particles.

The reproducibility of the DVB polymerization was tested by rotating three flasks with a monomer loading of 3% (v/v), whereas for the St-DVB polymerizations the reproducibility test was done with monomer concentrations of 2 and 4% (v/v). As shown in Table 3, the particles produced in the different vessels from the same polymerization mixtures were almost identical.

Polymerization Time. For thermally initiated polymerization the particles reach a size of 2.5−3.0 μm during 24 h of polymerization. If the photopolymerization is aborted after 24 h of polymerization, the particles are considerably smaller ($D_n = 0.39$ μm) and highly polydisperse (Figure 5a), with a polydispersity index in this case of 1.52 and a yield of only 3.4%. When the polymerization was continued on the same monomer mixture (another flask in the same batch) to a total time of 64 h, the particle diameter grew to 1.48 μm with a yield of 10.1%, and the particles became essentially monodisperse ($U = 1.016$) (Figure 5b). We have seen that with the current setup it takes ∼48 h to achieve monodisperse particles, the size of which is dependent on the monomer or initiator concentrations, as discussed above. Similar observations were made for all monomer concentrations tested; when monodispersity had been reached, continued polymerization on the same reaction mixture gave an increase in size with maintained monodispersity (Figure 6). Changes in the polymerization time could thus be used to fine-tune the size of a batch of the monodisperse particles. For particles polymerized for 163 h with 4% (v/v) DVB as monomer the average particle diameter was about 3.1 μm. For St-DVB particles prepared under identical conditions, the average diameter was 3.7 μm.

The yield, expressed as monomer conversion into particles, seemed to be almost linearly dependent on the polymerization time and was marginally influenced by the monomer concentration. For instance, the yield in a 2% DVB polymerization was 3.4% after 24 h, whereas a 4 and 6% DVB polymerizations showed conversions of 26.0 and 27.6% after 163 h (Table 1). Thermally initiated precipitation polymerizations usually achieve a yield of 60% after 24 h at 70 °C.

Surface Area and Morphology. The particles based on polymerizing DVB alone or in a 1:1 molar ratio with styrene differed in both surface area and porosity, as is evident from the nitrogen sorption/desorption curves in Figure 7. The St-DVB particles had low surface areas in the vicinity of 5 m^2/g that decreased with increasing particle size. They had some surface accessible pores that are in the low mesoporous range, with an average pore size varying from 3.7 to 4.5 nm. The pore volume on the other side was small, and if the adsorption isotherm is taken into consideration, the material behaves like a nonporous solid. Assuming a particle density of 1.1, the calculated external specific surface areas for samples 05-2-043/47 and 05-2-044/48 amounts to 33 and 45% of the measured areas. This estimate assumes perfectly smooth spheres, and we conclude that the particles are essentially nonporous since the external surface will not be molecularly flat.

The DVB particles have a more complex pore structure. During polymerization acetonitrile is presumably trapped inside the particles due to the rigid structure created by the heavy cross-linking. Because of this, it is difficult to reach equilibrium when measuring the surface area and pore size distribution. However, after an extensive preparation involving high vacuum at elevated temperature for at least 24 h, it was possible to carry out a surface characterization. The adsorption isotherms for samples containing DVB particles show an initial steep rise in the volume of gas adsorbed, and then it levels off to become almost horizontal. This indicates a microporous structure where the micropores are filled under relatively low pressure, and after that no adsorption takes place. A microporous structure also gives a higher specific surface area, which decreases the longer the particles are allowed to grow. The DVB particles had surface areas ranging from ∼150 m^2/g for particles with an average diameter of 1.5 μm to roughly 20 m^2/g for particles of 3.9 μm.

Conclusions

Highly cross-linked coagulum-free spherical DVB and St-DVB particles can be prepared by photoinitiated precipitation polymerization at monomer concentrations as high as 8 vol %. Photopolymerization offers a straightforward and interesting alternative to the more established thermal initiation since polymerization can be carried out at low temperature with corresponding lower tendencies of aggregate formation and also allows the polymerization temperature and initiation rate to be varied independently. The polydispersity index was below 1.022 for all polymerizations that were allowed to proceed for more than 40 h, and in some cases polydispersity indexes as low as 1.002 were obtained. For a given set of monomer and initiator concentrations, the polymerization time could be used to control the particle size with great precision. The yield increased in an almost linear fashion over time with a low yield of 3.4% after 24 h to 26.0% after 163 h of polymerization.

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