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ARTICLE

Preparation of Divinylbenzene and Divinylbenzene-*co*-Glycidyl Methacrylate Particles by Photoinitiated Precipitation Polymerization in Different Solvent Mixtures

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ABSTRACT: Highly cross-linked micrometer-sized polymer particles with intended use in liquid chromatography were made from divinylbenzene, alone or copolymerized with 2,3-epoxypropyl methacrylate, using photoinitiated precipitation polymerization. The polymerizations were made by irradiation from a 150 W short arc xenon lamp with 2,2′-azobis(2-methylpropionitrile) as initiator. A variety of solvents such as tetrahydrofuran (THF), toluene, 1-decanol, and 1-octadecanol were added to the polymerization mixture, singly or in combination with THF, in order to introduce and control the porosity of the particles. Polymerizations where cosolvents were used in combination with the near-Θ solvent acetonitrile resulted in a substantial increase in particle size. This made it possible to shorten the polymerization time while still obtaining particles in the desired size range of 2−5 μm. Scanning electron micrographs indicated that the particles prepared by addition of "good" cosolvents had what seemed to be a softer surface. The materials were packed into analytical columns at 60 MPa packing pressure and passed a pressure stability test up to 30 MPa pressure drop. Darcy's law plots revealed that the columns had no tendencies for compression-induced back-pressure variations or bed collapse.

Introduction

Micron-sized polymer particles have long been used as chromatographic separation materials, and their preparation has taken place by a variety of polymerization schemes, including emulsion, dispersion, and precipitation polymerizations.[1−3] Precipitation polymerization is a way to synthesize monodisperse highly cross-linked particles in the 1−5 μm size range, which is often practiced using divinylbenzene (DVB) as a cross-linker without the use of steric stabilizers or surfactants.[2,4,5] The prevailing trend in liquid chromatography is toward shorter and narrower columns, packed with sub 3 μm particles that can withstand very high pressure. Particles prepared from 55% or 80% technical grade DVB isomers as the sole monomer are very rigid, and their extreme cross-linking makes them resistant to high temperature[6] and pressure[7] and warrants chemical stability over the entire aqueous pH range. This makes them suitable as support in chromatographic separation columns and a chemically more stable alternative to the more commonly used silica materials.

In precipitation polymerization, the monomer and initiator are soluble in the solvent (e.g., acetonitrile), and in the polymerization process, soluble oligomers aggregate to form small clusters of polymers. When the particles have reached sufficient mass, they precipitate out of solution, and by continuously tumbling the reaction vessel, these macroparticles can capture more oligomers for further growth.[8] The high amount of cross-linker used in precipitation polymerization makes the particles self-stabilized, with a surface consisting of a styrenic polymer with pendant ethyl and vinyl groups. Unpolymerized vinyl groups cover the surface and serve as useful handles for further functionalization. Reaction with thiols by grafting to, attaching a halide to the vinyl group and grafting from the surface, or to start a second polymerization in a core−shell fashion are just some methods used for functionalization of DVB particles.[9−13] Numerous methacrylates have been copolymerized with DVB as cross-linker, and this has proven to be a viable way of achieving different surface functionalities.[4] Lightly cross-linked particles of 2-hydroxyethyl methacrylate have, e.g., been used as a starting point for grafting of various methacrylates from the surface by atom transfer radical polymerization (ATRP) after additional reaction with 2-bromopropionyl bromide.[10,14,15] Polymerization with incorporation of methacrylic acid as the functional monomer together with a template molecule has been used for making molecularly imprinted polymer (MIP) particles.[16,17] If 2,3-epoxypropyl methacrylate (GMA) is added as a second monomer to the polymerization mixture, the surface will also contain oxirane groups which provide alternative ways for functionalization and creation of new surface morphologies.[18] Copolymerization of GMA with DVB as cross-linker is thus of great interest for chromatographic purposes due to the high rigidity and stability. Particles containing GMA on the surface have been prepared in a one-step precipitation polymerization in acetonitrile, by dispersion polymerization in alcohol, or by a surface grafting onto silica gel.[19−22]

The solvent used in precipitation polymerization has predominantly been acetonitrile (Hildebrand solubility parameter, δ = 24.3 MPa$^{1/2}$) since it meets the requirement of being a near-Θ solvent, even at ambient temperature.[23] Recently Yang et al. described precipitation polymerization of DVB in acetic acid (δ = 20.9 MPa$^{1/2}$) at temperatures of 60−80 °C with similar results as for acetonitrile.[24] Some other exceptions have also been reported, where the main goal has been to create porous microspheres with a higher surface area, and the solvent most frequently used as a porogen has been toluene (δ = 18.2 MPa$^{1/2}$).[25,26] Particles produced in systems containing porogens have been used in chromatography both for separation of small molecules in enthalpic interaction modes and as separation materials in size exclusion chromatography.[25,27]

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We have previously reported on the synthesis of highly cross-linked and nonporous particles from DVB and styrene-*co*-DVB, which can be made exceptionally monodisperse when the precipitation polymerization is carried out by photoinitiation.[28] In our efforts to further develop and investigate the technique of photoinitiated precipitation polymerization for production of materials suitable for use as stationary phase supports in liquid chromatography, we have in this work incorporated various solvents into the polymerization mixture to determine if this could result in higher pore volumes and larger pore sizes. The incorporation of GMA was also made to render the particles less hydrophobic and to provide an alternative type of handle on the surface for modifications by different grafting approaches.

Experimental Section

Chemicals. DVB (technical grade consisting of 80% DVB isomers and ethylvinylbenzene as balance) and GMA were from Fluka (Buchs, Switzerland). Both monomers were freed from inhibitors by passing them through basic Al_2O_3 (Brockmann grade I; Aldrich, Schnelldorf, Germany). The initiator 2,2′-azobis(2-methylpropionitrile) (AIBN; Serva, Heidelberg, Germany) was used as received and kept in a freezer until use. Acetonitrile (Fisher Scientific, Loughborough, UK), tetrahydrofuran (J.T. Baker, Deventer, Holland), and toluene (Merck, Darmstadt, Germany) were all of analytical grade and dried with 3 Å molecular sieves (VWR International, Spånga, Sweden). Other solvents and chemicals used in the polymerizations were 1-octadecanol and 1-decanol (Fluka), both used as received. Organic solvents such as acetone (BDH, Poole, UK) and methanol (J.T. Baker) were analytical grade and used without further purification. Uracil was purchased from Fluka, methanol for chromatography was of HPLC grade (J.T. Baker), and the water used for preparation of eluents was prepared by Ultra-Q equipment (Millipore, Bedford, MA) and has a resistivity of > 15 MΩ·cm.

Polymerization. The photoinitiated precipitation polymerization of DVB was carried out in a similar way as reported previously, using polypropylene flasks.[28] In a typical polymerization 7.31 g of DVB (8 mL, 56 mmol, 4% v/v of the solvent) was added to the flask together with 200 mL of dry solvent (acetonitrile and porogen) followed by 0.146 g (0.9 mmol) of AIBN initiator (2% w/w of monomer). In the polymerizations where 1-octadecanol was used as porogen, 1.0 g was dissolved in 40 mL of THF, giving a total cosolvent volume in the polymerization of ~20%. The mixture was shaken to dissolve the initiator and degassed by nitrogen purging for ~10 min to remove dissolved oxygen. The flasks were attached to a rotor, four at the time, and tumbled along their long axes at 15 rpm. A 150 W short arc xenon lamp was focused onto the flasks cluster, and the polymerization time was varied from 46 to 96 h as listed in Tables 1 and 2. After polymerization the solvent and unreacted monomer were filtered off using 0.45 μm nylon membrane filters, and the harvested particles were washed successively with THF and acetone. The washed particles were dried under partial vacuum (~2 kPa) at 40 °C for 24 h. For copolymerization of DVB-*co*-GMA the ratios of cross-linker used in the experiments were calculated from the molar amounts of GMA and DVB added, and under typical conditions the molar ratio was 1:1. The monomer concentration with respect to solvent, the initiator concentration with respect to the total monomer concentration, and the procedure were the same as above.

Characterization. Scanning electron microscopy (SEM) was used to evaluate the size of the particles and their morphology before and after they had been packed into a chromatographic column under high pressure. Particles (virgin or unpacked from the column following the pressure test; see below) were placed on sticky carbon tape attached to alumina stubs (Agar Scientific Ltd., Stanstead, UK) and evaporation-coated with ~15 nm of gold and carbon in a Edwards E12 vacuum coating unit (Edwards High Vacuum Ltd., Crawley, UK). Scans were made on a Cambridge 360ixp microscope run with a LaB_6 electron emitter (Leica Cambridge Ltd., Cambridge, UK) on randomly selected particle populations and at different standardized magnifications. From these micrographs, 100 particles were counted to get an estimation of the number-average diameter.

Table 1. Polymerizations of Divinylbenzene (4% v/v) with Different Cosolvents in Acetonitrile for 96 h

cosolvent[a]	solubility parameter[34] ($MPa^{1/2}$)	surface area (m^2/g)	pore size (nm)	pore volume (cm^3/g)	polymer shape
toluene	18.2	29.8	5.90	0.008	polydisperse particles
tetrahydrofuran (THF)	18.6	22.6	6.91	0.008	monodisperse particles
octadecanol in THF		486	2.53	0.12	narrow disperse particles
1-decanol	20.5	429	2.70	0.12	monodisperse particles

[a] A cosolvent volume of 10% compared to acetonitrile except for octadecanol dissolved in THF where the used volume was 20%.

Table 2. Polymerizations of Divinylbenzene with Different Concentrations of Tetrahydrofuran (THF) as Cosolvents

THF (%)	time[a] (h)	particle size[b] (μm)	U[c]	CV[d] (%)	surface area (m^2/g)	pore size (nm)	pore volume (cm^3/g)	yield[e] (%)
0	48	0.8	1.033	10.7	45.3	6.81	0.04	11.5
10	46	3.5	1.003	3.1	22.6	6.91	0.008	13.1
20	46	4.6	1.004	3.8	19.9	8.13	0.005	14.0
30	46	4.7	1.109	18.9	410	2.42	0.13	11.4
40	46	5.1	1.006	4.5	562	2.89	0.17	13.2

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

Multipoint surface area and porosity measurements were made with a Tristar 3000 (Micromeritics, Norcross, GA) automated adsorption unit and calculated from the nitrogen adsorption isotherm using the Brunauer−Emmett−Teller (BET) equation.[29] Prior to analysis the sample (~100 mg) was heated to 120 °C under a continuous flow of nitrogen for at least 3 h in a Micromeritics SmartPrep degassing unit. Measurements were made in the dry state, and the pore size distribution and pore volumes were calculated based on the Barrett−Joyner−Halenda (BJH)[30] scheme, which assumes that the pores have cylindrical shapes.

Preparation of the Particles for Pressure Test. To test the pressure stability of the DVB and DVB-*co*-GMA particles, they were slurry packed into stainless steel analytical column blanks with an inner diameter of 2.1 mm and 50 mm in length (Applied Porous Technologies, Tariffville, CT) using methanol as solvent. A pneumatic amplifier type HPLC pump (Knauer, Berlin, Germany) was used to slowly increase the packing pressure from an initial value of 10 to 60 MPa during the course of 3 h. The maximum pressure was maintained for 60 min before it was gradually decreased and the column capped. Following the packing, the columns were connected to a Bischoff (Leonberg, Germany) model 2250 HPLC pump to measure the pressure drop over the packed bed. The specific permeability was calculated according to Darcy's law:

$$u = \frac{\Delta P K_0 {d_p}^2}{\eta L} \qquad (1)$$

where u is the flow velocity, ΔP the column pressure drop, K_0 the specific permeability, d_p the average size of the particles, η the viscosity of the test solvent (eluent), and L the length of the

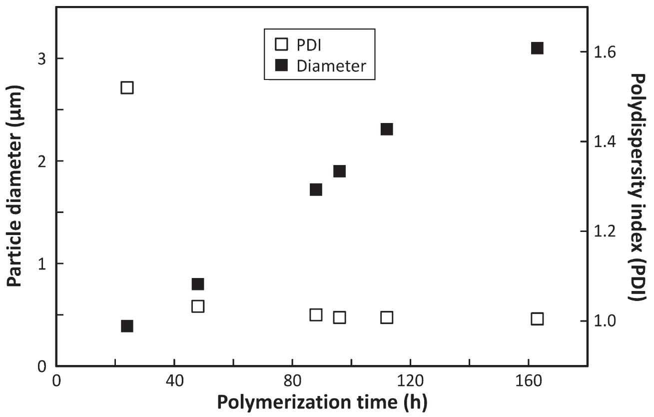

Figure 1. Polymerizations of divinylbenzene particles prepared with 4% (v/v) monomer and 2% (w/w) initiator in acetonitrile. The average particle size has been plotted against the polymerization time to show the almost linear growth in diameter with time, along with a concurrent decrease in polydispersity index.

column. The system was run isocratically with an eluent consisting of methanol−water (4:1, v/v), with uracil injected as void marker. The pressure drops over the columns were recorded from the built-in pressure sensor of the pump. After the pressure tests, the columns were unpacked and the particles dried in vacuum before being subjected to scanning electron microscopy.

Results and Discussion

Polymerization. Precipitation polymerization is a scheme that is suitable for UV initiation since the preferred solvents are transparent in the wavelength region of interest (300−400 nm). With the setup used in these experiments, the polymerization mixture was not actively thermostated. It therefore adsorbed heat from the focused xenon lamp that was placed at a distance of 30 cm, causing a temperature rise of ~10 °C above ambient and an effective polymerization temperature of 30−32 °C. Under these conditions, the mixture started to turn milky due to the formation of particulate polymer after 2 h of polymerization. This turbidity may cause a reduction in the penetration depth of the UV irradiation, but the constant tumbling of the reaction vessels allows oligomers to come close to the wall, so that the polymerization can continue homogeneously throughout the suspension. This attenuation could be one of the reasons for the relatively slow conversion in photoinitiated precipitation polymerization, and it therefore needs a relatively long polymerization time to result in a particle size (1.5−5 μm) suitable for high-performance liquid chromatography. The slow growth of the particles prevents aggregation and coagulum formation, and the particle diameter shows a remarkable linear growth during an entire week of polymerization, as shown in Figure 1. The polydispersity index plotted in the same graph shows that the particles also become increasingly monodisperse with increased polymerization time. For DVB (4% v/v) polymerized in acetonitrile for 48 h with 2% (w/w) of initiator, the average particle size was only 0.8 μm. When the polymerization was continued, the particles continued to grow, reaching an average particle size of 3.1 μm after 163 h. The particle growth trendline has a slope of 0.48 μm/day ($r^2 = 0.986$), which can be used to compare the particle size growth rate in the polymerizations where other solvents were added to the polymerization mixture. The particles produced in acetonitrile without addition of cosolvent had a relatively high surface area, where the majority came from micropores, i.e., pores <2 nm in diameter, as measured by the BET principle. Pores of this size are too small to allow efficient solute diffusion, and the particles will therefore behave essentially as nonporous when used in a liquid chromatographic setting, provided the surface is sufficiently well shielded by a dense graft layer.

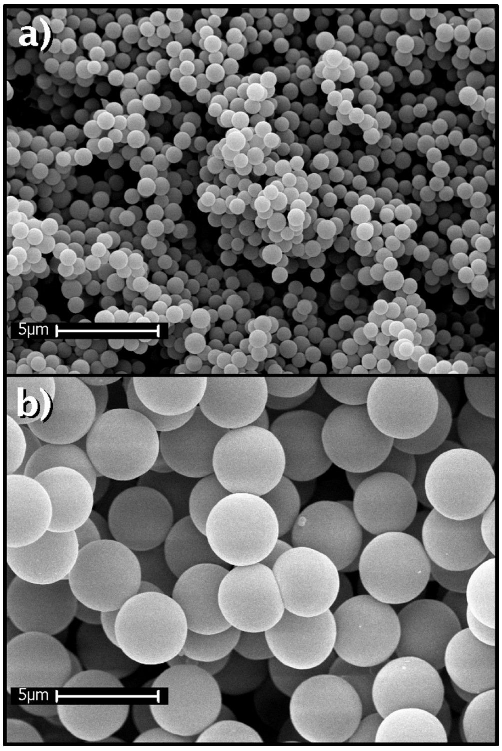

Figure 2. Scanning electron micrographs at identical scale for divinylbenzene particles polymerized for (a) 48 h in acetonitrile only and (b) 46 h in acetonitrile with 10% tetrahydrofuran (THF) added, showing the increase in size as a result of adding THF as cosolvent.

Addition of Cosolvents. In an effort to create particles with a higher porosity and different surface morphology, cosolvents were mixed together with acetonitrile to alter the Θ-value of the solvent. DVB was chosen as monomer, since it is the most frequently used monomer in precipitation polymerization. When polymerized in acetonitrile, DVB is known to produce monodisperse particles so the experiments started with only 10% of cosolvent, not to alter the solubility parameters too far away from pure acetonitrile. Four solvents listed in Table 1, some that had previously been used as porogens in the preparation of monoliths[31,32] or in polymerization of other types of particulate porous supports for chromatographic stationary phases were tested in photoinitiated precipitation polymerization. In the polymerization where toluene was added as cosolvent, the particles were still polydisperse after 48 h of polymerization. Although the results above show that extension of the polymerization time led to higher monodispersity for photoinitiated precipitation polymerization with acetonitrile as the only solvent, a trend in this direction was not observed for polymerization in acetonitrile/toluene mixture, even after an additional 48 h of polymerization. Previous polymerizations that have reported monodisperse particles resulting from a solvent system of acetonitrile/toluene have been carried out by thermal initiation at an elevated temperature of 70 °C.[25] At this temperature the solvent mixture behaves as a Θ-solvent, but since the Θ-value is depending on the temperature, toluene may not have the correct cosolvent properties to result in monodisperse particles at near ambient temperature.

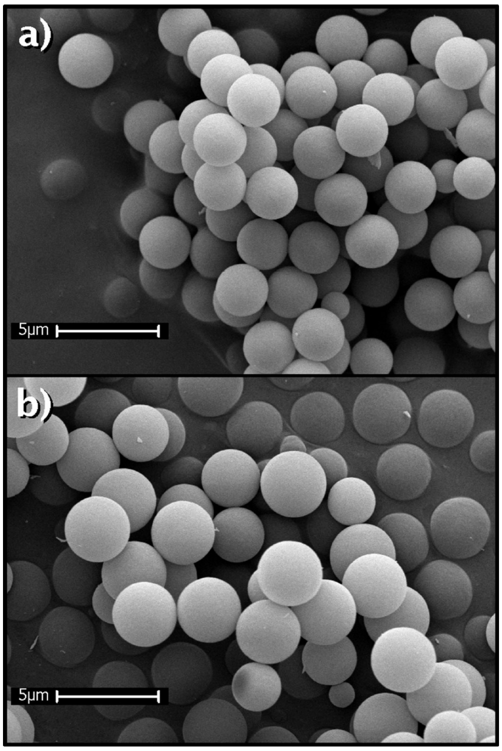

Figure 3. Divinylbenzene particles polymerized for (a) 96 h in acetonitrile with 20% 1-decanol as cosolvent and (b) for 137 h in acetonitrile with 1-octadecanol dissolved in tetrahydrofuran to give a total cosolvent volume of 20%.

The polymerization with 10% THF added as cosolvent showed very promising results, not only by a high level of monodispersity but also a substantially faster particle size growth. Under otherwise identical conditions, the particle diameter grew 4 times faster in the presence of THF compared with only acetonitrile as solvent (Figure 2). This polymerization with 10% THF as cosolvent was so encouraging that it was continued with admixture of 20, 30, 40, and 50% (v/v) THF in acetonitrile. It was observed that the particle diameter growth rate continued to increase up to 40% (v/v) THF (Table 2). When 50% THF was added, the polymer remained soluble in the polymerization solution and never precipitated. Monodispersity was achieved with THF fractions of 10, 20, and 40% THF, whereas the particles prepared with 30% THF as cosolvent showed a broad size distribution between 3.0 and 6.6 μm, with a polydispersity index above 1.1. Particles polymerized with 40% THF had an average size of 5.1 μm after 46 h of polymerization, and the SEM images showed some irregularities which were interpreted as arising from a soft surface. When 10 and 20% THF were added, both the surface area and pore volume decreased. From the N_2 adsorption isotherms, these materials appeared to be essentially nonporous, similar to the particles polymerized without THF. Admixture of THF up to 20% (v/v) therefore appears to be a viable way of speeding up the polymerization 5 times, without significantly altering the porous properties. At higher THF percentages, the surface area increased substantially, as did the pore volume. The pore size distribution, on the other hand, showed a shift toward smaller diameters, with adsorption isotherms characteristic of a microporous structures. Concomitant increase in surface area and decrease in pore size could indicate that more solvent is trapped in the particle formation due to the formation of a soft gel type layer in a solvent mixture containing a significant fraction of the better solvent THF. Because this process is expected to prevail during the entire polymerization, the pore system will consist of a deep and narrow pore system with an average pore size between 2 and 3 nm. Such pore systems are not useful in liquid chromatography. The rate of monomer consumption at different THF admixtures also turned out to be essentially identical since the yield of particles varied

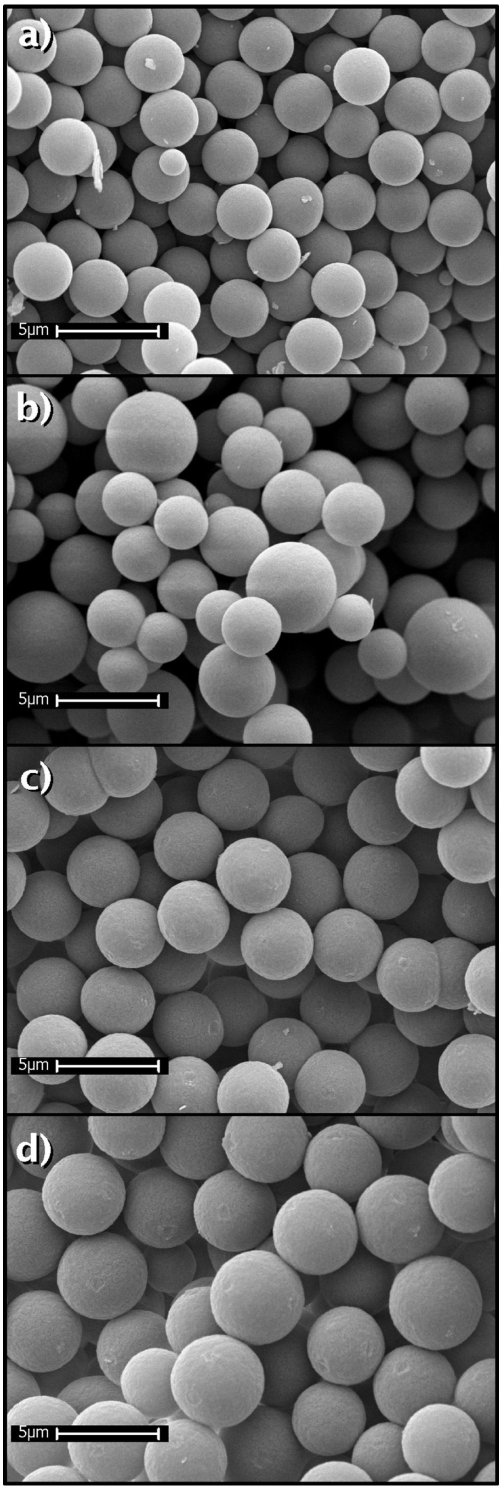

Figure 4. Particles consisting of divinylbenzene-*co*-2,3-epoxypropyl methacrylate in a molar ratio of 1:1 polymerized with different solvent mixtures where (a) is 2% (v/v) monomer in acetonitrile, (b) is 4% (v/v) monomer in acetonitrile, (c) 4% (v/v) monomer in acetonitrile with 5% tetrahydrofuran (THF) and 5% 1-decanol, and (d) 4% (v/v) monomer in acetonitrile with 10% THF.

Table 3. Polymerizations of Divinylbenzene-*co*-2,3-Epoxypropyl Methacrylate in Acetonitrile with Different Monomer Concentrations and Addition of Cosolvents

cosolvent	monomer[a] (%)	time[b] (h)	particle size[c] (μm)	U[d]	CV[e] (%)	surface area (m^2/g)	pore size (nm)	pore volume (cm^3/g)
none	4	96	3.3	1.193	25.8	2.65	11.0	0.005
none	2	96	2.7	1.019	9.6	3.38	12.0	0.006
tetrahydrofuran (THF)	4	48	4.1	1.013	6.5	2.54	15.4	0.004
THF/1-decanol	4	48	3.6	1.003	3.3	2.18	14.8	0.004

[a] Total monomer concentration in regards to solvent. [b] Polymerization time. [c] Number-average particle size. [d] Polydispersity index D_w/D_n. [e] Coefficient of variation.

between 11.4 and 14.0 wt % of the loaded monomers (Table 2). This means that the larger particles polymerized with higher fractions of THF were more swollen. Some particles were also seen to have fused together when THF was used as cosolvent, as is evident from Figure 2b.

Monodisperse particles were also produced when 1-decanol was used as cosolvent, but the growth rate was much slower compared to using THF. The size difference between DVB particles polymerized with acetonitrile only as solvent or with addition of 1-decanol as cosolvent was a 0.6 μm increase in size after a polymerization time of 96 h. The other porogen tested in an attempt to increase the pore volume was 1-octadecanol dissolved in THF. This mixture made the particles grow more rapidly, but the resulting particles were only narrow disperse, as seen in Figure 3. There was almost no difference in surface area, pore size, or pore volume between 1-decanol and 1-octadecanol as porogen. Both long-chain alcohols resulted in high surface areas, but the adsorption isotherms showed that the pore sizes were in the microporous range.

Copolymerization of DVB and GMA. Monodisperse DVB-*co*-GMA particles are of interest as chromatographic material since the rigid particles become less hydrophobic and the oxirane group gives the possibility to use a variety of different anchoring techniques in the functionalization steps. Using the same method and setup as for polymerization of DVB resulted in a relative broad particle size distribution at a monomer concentration of 4% (v/v). When the monomer loading was decreased to 2% (v/v), it was possible to achieve monodisperse DVB-*co*-GMA particles. Again the conversion rate was slow, with 4 days needed to obtain particles in the size range of 3 μm, but copolymerization with GMA still resulted in a faster conversion rate than polymerization of DVB alone. As we reported previously for photoinitiated polymerization of DVB in acetonitrile, the particles were polydisperse in the beginning of the polymerization and grew monodisperse as they continued to capture oligomers.[28] In this case the particle size distribution as a function of polymerization time seemed to have more to do with the monomer loading in combination with a too high fraction of GMA. Previous studies of DVB-*co*-GMA particles by precipitation polymerization have shown similar results, that the polydispersity tends to increase with higher monomer concentration.[4,19] In our investigation we used a molar ratio of 1:1 between DVB and GMA which has been unsuccessful in giving monodisperse particles according to previous studies. The polydispersity for a monomer loading of 4% (v/v) in photoinitiated precipitation polymerization could be due to polymer particles sticking to the wall of the reaction flask and thereby preventing further growth for some particles. In the process of cleaning the particles the flasks were shaken to disperse the precipitated particles, and thereby also particles stuck to the wall were released and collected.

Since the polymerization of DVB when using 10% of THF as cosolvent showed an enhanced particle growth rate, it was also tested for copolymerization of DVB-*co*-GMA. First results showed that a monomer loading of 4% (v/v) could be used to achieve monodisperse particles with THF as cosolvent (Figure 4). The particles with THF grew faster, reaching the average size of 4.1 μm in 48 h, compared to 96 h for particles polymerized without THF. An experiment with a ternary system was made where 5% 1-decanol was added together with 5% THF to the solvent, since 1-decanol resulted in monodisperse particles for DVB. These particles were also monodisperse, but they did not grow to the same size as when only THF was added, as summarized in Table 3. There is a clear indication that the particles grow faster with more THF as cosolvent, and the reason for this faster growth is not clear at present. The surface of the DVB-*co*-GMA particles was smooth and appeared essentially nonporous at the highest image resolution attainable with the scanning electron miscoscope. Particles polymerized with THF showed a small increase in surface area from 2.2 to 3.3 m^2/g, and the calculated specific surface areas assuming, a density of 1.1, would be 2.4 and 1.6 m^2/g, respectively.

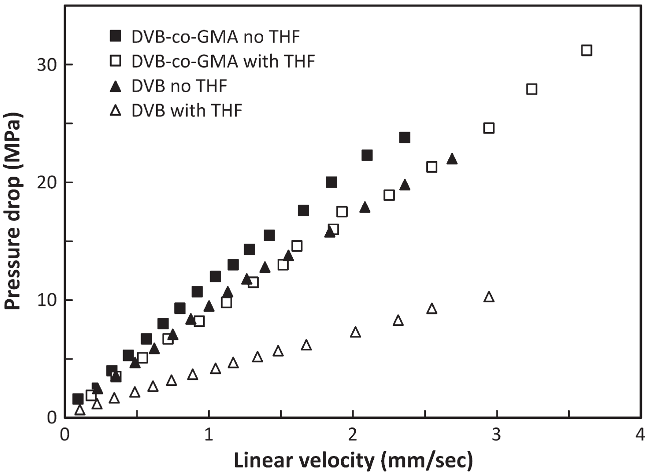

Figure 5. Pressure drop over the 50 mm long by 2.1 mm i.d. stainless steel columns packed with particles prepared with and without tetrahydrofuran as cosolvent as a function of the superficial linear flow velocity, using methanol−water (4:1, v/v) as eluent.

Material Compressibility. If the particles are to be used as base material in high-performance liquid chromatography, the packed bed will have to withstand high pressure without being compressed or collapse. From the SEM micrographs taken directly after the synthesis, it appeared as if there was a tendency for particles polymerized with fractions of THF as cosolvent to be compressible due to gel-like surface properties caused by the good solvent. DVB and DVB-*co*-GMA particles prepared with and without THF as cosolvent were therefore packed in 5 cm columns using a maximum packing pressure of 60 MPa, followed by a compressibility test in a chromatography system run with methanol−water (4:1, v/v) as eluent. The linear back-pressure vs flow rate curves in Figure 5 had no hysteresis and showed no signs of the material compression or a bed collapse when subjected to pressure drops of up to 30 MPa.

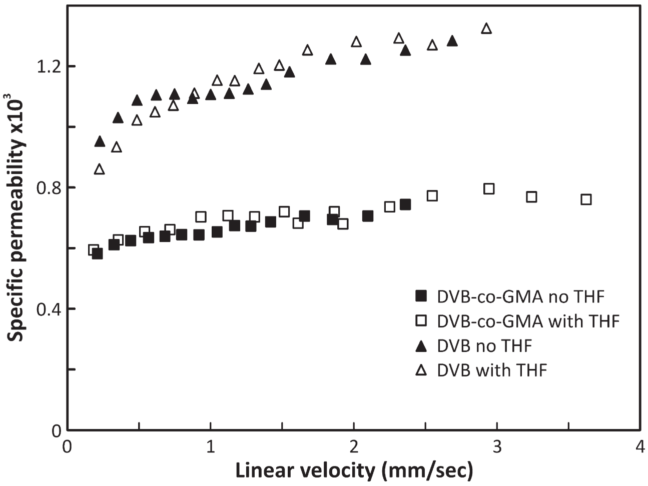

Figure 6. Permeabilities for columns packed with divinylbenzene (DVB) and DVB-*co*-2,3-epoxypropyl methacrylate particles polymerized with acetonitrile alone and acetonitrile with tetrahydrofuran added as cosolvent.

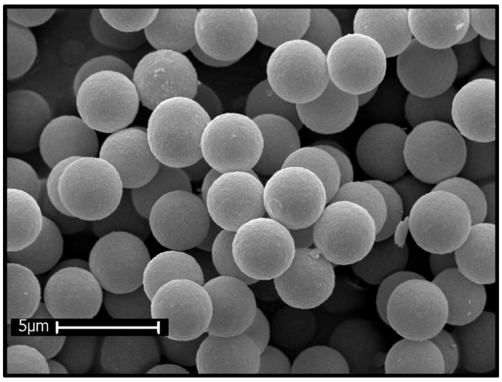

Figure 7. Scanning electron micrograph of divinylbenzene-*co*-2,3-epoxypropyl methacrylate particles that were subjected to a packing pressure of 60 MPa in methanol and a flow permeability test in methanol/water (4:1, v/v), showing no evidence of damage after unpacking.

The permeability of the packed columns was measured with the same methanol–water eluent (4:1, v/v), having a viscosity of 1.112 cP at 25 °C.[33] The particles behaved in the same way whether they were polymerized with THF as cosolvent or not, and the specific permeabilities were grouped corresponding to the materials of which the particles were made (Figure 6). The DVB-*co*-GMA particles had a lower permeability which is expected since the degree of cross-linking is not as high. This could also depend on the surface of the particles since the specific permeability is based on the particles being nonporous. This is not completely true since DVB particles have a microporosity with a moderately high surface area and the DVB-*co*-GMA has a mesoporous structure with a very low surface area; however, none of the particles can be suspected of supporting an internal hydraulic flow. At low flow rates the specific permeabilities appear to drop slightly, but we attribute this to the pump not being able to supply eluent properly at low flow rates or a nonlinearity in the built-in pressure gauge. After the columns were pressure tested, the material was removed from the columns and scanned with SEM (Figure 7). There recovered particles showed no signs of having been compressed, dented, or cracked during the pressure tests.

Conclusions

Monodisperse DVB and GMA-*co*-DVB particles were prepared by photoinitiated precipitation polymerization in acetonitrile, neat or with additions of THF and 1-decanol as cosolvents. Addition of 1-octadecanol dissolved in THF gave narrow dispersed particles. A substantial improvement in particle growth was seen when THF was used as cosolvent, providing a possibility of cutting the polymerization time by more than half. In 46 h, particles sizes well above 3 μm were reached for both pure DVB and GMA-*co*-DVB. The surface area for DVB particles changed with the amount of THF, but from a chromatography perspective they will still be considered as nonporous. Increasing the fraction of THF cosolvent led to a larger pore volume and an increasing surface area, whereas the pore size decreased. A similar effect with larger pore volume and narrower pore size was seen with 1-decanol as cosolvent. The particles were capable of withstanding a packing pressure of up to 60 MPa in 5 cm long columns without showing physical signs of damage, and the beds packed at this pressure showed no compressability according to Darcy's law plots.

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