Growth Mechanism of Poly(divinylbenzene) Microspheres in Precipitation Polymerization

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ABSTRACT: The residual surface vinyl groups in poly(divinylbenzene) microspheres prepared by precipitation polymerization in acetonitrile were converted to hexyl groups by treatment with *n*-butyllithium and to ethyl groups by catalytic hydrogenation in the presence of Wilkinson's catalyst. These modified particles and unmodified particles were used as seeds in separate precipitation polymerizations of divinylbenzene in acetonitrile, under identical conditions. Only the unmodified seeds were able to capture the oligomers formed and grow without secondary initiation. Both the butylated and the hydrogenated samples showed extensive secondary initiation instead of seed particle growth. These results demonstrate that precipitation polymerization of divinylbenzene in near-Θ solvents is an entropic precipitation, involving radical reactions between the macromonomer particles and newly formed oligomers. These results further imply that the growing particles are autostabilized by the transient solvent-swollen gel layer on their surfaces, formed by a recently captured oligomer.

Introduction

The wide range of commercial applications for polymer microspheres has encouraged much recent research in this field. In particular, microspheres of uniform size and shape are being used as functional supports,[1] as chromatographic separation media,[2,3] and in other areas.[4−6]

The polymerization methods available to prepare such monodisperse microspheres, such as water-based emulsions, seeded suspension polymerizations, nonaqueous dispersion polymerizations, and precipitation polymerizations, have been reviewed recently.[6−8,9]

Precipitation polymerizations are unique within this group in that they can lead to monodisperse microspheres free of any added surfactant or stabilizer.[10−17] This paper addresses the mechanisms of microsphere growth and colloidal stabilization during the precipitation polymerization of divinylbenzene in organic solvents.

Precipitation polymerizations start as homogeneous mixtures of monomer, initiator, and, optionally, solvents.[11,14−16,18] During polymerization, the growing polymer chains phase-separate from the continuous medium by *enthalpic* precipitation, in cases of unfavorable polymer−solvent interactions, or *entropic* precipitation, in cases where cross-linking prevents the polymer and solvent from freely mixing.[19] The bulk polymerizations of vinyl chloride and acrylonitrile are classic examples of enthalpic precipitation polymerizations where the propagating chains grow beyond their solubility limit in the organic medium, which may be the monomer itself, and precipitate. The resulting nuclei typically aggregate into larger, polydisperse particles that continue to grow by capturing other particles, by newly formed polymer chains, or by absorption and polymerization of monomer.

We are particularly interested in entropic precipitation polymerizations, i.e., those carried out in the presence of both a cross-linker and a solvent for the polymer. In good solvents, these polymerizations will often produce turbid macroscopic or microscopic gels, depending largely on the original monomer concentration.[20−28] In poorer solvents, precipitation polymerization normally produces micrometer-sized particles.[10−16,18] Their size distribution is often broad due to a lack of colloidal stability.[6]

Recently, we reported on the formation of monodisperse poly(divinylbenzene) microspheres by precipitation polymerization of divinylbenzene in acetonitrile in the presence of AIBN, a radical initiator.[11] Similar but porous monodisperse microspheres were formed by polymerization in a mixture of acetonitrile and toluene.[12] The narrow particle size distributions observed resemble those found in dispersion polymerizations, suggesting the particles become colloidally stable early on in the polymerization. Previous reports on the use of precipitation polymerization to prepare monodisperse spherical particles are limited. Naka and co-workers reported on both the AIBN and the ^{60}Co γ-ray-initiated polymerizations of diethylene glycol dimethacrylate (DEGMA) in a variety of organic solvents.[13] Monodisperse particles were obtained only using γ-ray initiation, while AIBN initiation yielded particles with broad size distributions. In both the divinylbenzene and the DEGMA systems, the mechanism of particle growth and colloidal stabilization in the absence of an added stabilizer remained unclear, although Naka suggested the DEGMA polymer microspheres grow by reacting with a portion of the oligomer formed in solution and with monomer. However, the DEGMA microspheres were formed in good solvents, suggesting entropic precipitation, while the polymerization of DVB-55 in good solvents such as toluene leads to microgels and space-filling gels only.[28] Near-Θ solvents such as acetonitrile[11] or acetonitrile/toluene mixtures[12] are required to form distinct poly(DVB) microspheres of 2−5 μm diameter. The fact that both DEGMA and DVB systems require cross-linking monomer to form microspheres does indicate a critical role for the cross-linker, in both growth and stabilization.

Dispersion polymerization is closely related to precipitation polymerization; however, steric stabilizers are added to the dispersion system to control the size and narrow the size distribution of the particles.[4] As well, the presence of as little as 0.3−0.7% cross-linker relative

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to monomer in a dispersion polymerization leads to a broad size distribution, since the grafted stabilizer becomes buried within the particle.[29-32]

Hence, monodisperse styrenic microspheres may be prepared by several techniques, two of which are (i) dispersion polymerization, in the presence of added steric stabilizer but without significant amounts of cross-linker, and (ii) precipitation polymerization, in the presence of cross-linker but without added steric stabilizer. These criteria clearly indicate that the mechanisms of particle growth and stabilization in precipitation polymerization differ considerably from those active in the more established dispersion polymerization.

Two questions arise in relation to the precipitation polymerization of divinylbenzene to form microspheres: First, how do they nucleate and, in particular, grow? Second, how are the growing microspheres colloidally stabilized? In this paper we examine the critical role of residual surface vinyl groups in these processes, by conducting precipitation polymerizations involving microspheres with and without surface vinyl groups as seed particles.

Experimental Section

Materials. Technical grade divinylbenzene (DVB-55), containing 55% of the para- and meta-divinyl isomers and 45% of the para- and meta-ethyl vinyl isomers, was obtained from Aldrich Chemical Co. HPLC grade acetonitrile, toluene, and tetrahydrofuran (THF) were purchased from Caledon Chemical and used as received. 2,2′-Azobis(2-methylpropionitrile) (AIBN) was purchased from DuPont and recrystallized from methanol prior to use. Wilkinson's catalyst (tris(triphenylphosphine)rhodium chloride) and *n*-butyllithium (1.6 M in hexane), both from Aldrich Chemical Co., were used for particle modification.

Microsphere Preparation. DVB-55 (36.0 mL, 251 mmol), acetonitrile (900 mL), and AIBN (0.657 g, 4.00 mmol) were placed within a 1 L polyethylene bottle and shaken vigorously for several minutes to ensure complete dissolution of the initiator. The polymerizations were conducted by placing the bottles within a reactor connected to a programmable temperature controller capable of maintaining the set temperature to within ±1 °C. The reactor gently agitates the sample by rolling the bottles in a horizontal position at approximately 4 rpm. The temperature profile used for the polymerizations started with a 1 h ramp from room temperature to 60 °C followed by a 1 h and 40 min ramp to 70 °C. Once at 70 °C, the reactions were continued for 24 h. The highly cross-linked particles were isolated by vacuum filtration over a 0.5 μm membrane filter with three subsequent washings with tetrahydrofuran (THF). The washed microspheres were dried at room temperature under vacuum for 24 h. The particles were then analyzed by Fourier transform infrared (FT-IR) spectroscopy, Coulter multisizer, and environmental scanning electron microscopy (ESEM).

Butylation Reaction. A 250 mL, three-necked, round-bottom flask was evacuated, flame-dried, and purged with dry nitrogen. With nitrogen flowing through the apparatus, a charge of unmodified particles (5.08 g) was placed within the flask. The system was repeatedly evacuated and purged with dry nitrogen. Toluene (200 mL) and THF (20 mL) were added to disperse the particles, and the mixture was stirred magnetically. A solution of *n*-butyllithium in hexanes (30 mL, 48 mmol) was added quickly to the dispersion, producing an orange-red mixture. The reaction was allowed to proceed for 12 h at room temperature and was then quenched by addition of methanol. The particles were isolated from the reaction mixture by vacuum filtration over a 0.5 μm membrane filter. They were washed with methanol and THF to remove lithium methoxide and dried for 24 h under vacuum to yield 5 g of white particles. These butylated particles were analyzed by FT-IR, Coulter multisizer, and ESEM.

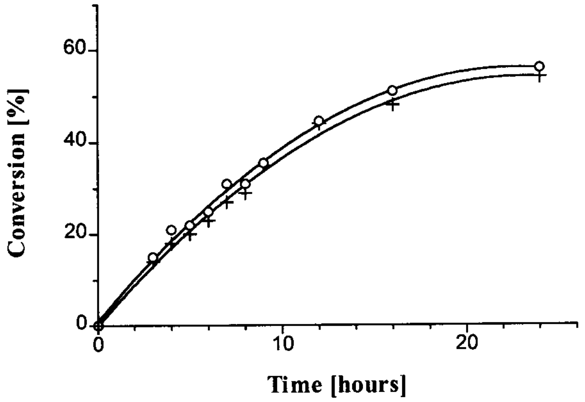


Figure 1. Conversion of monomer to particles (○) and to total polymer (+). The difference between the conversion to particles, and conversion to total polymer, corresponds to the soluble polymer fraction.

Catalytic Hydrogenation. Unmodified particles (10.0 g), toluene (100 mL), and tris(triphenylphosphine)rhodium chloride (0.100 g, 0.108 mmol) where placed within a Parr shaker apparatus which was subsequently charged with 2.5 atm of hydrogen pressure.[33] The reaction was allowed to proceed at room temperature with shaking for 3 days. The resulting hydrogenated microspheres were isolated by vacuum filtration and washed with toluene and THF to remove catalyst residues. The washed particles were dried under vacuum at room temperature and were analyzed by FT-IR, Coulter multisizer, and ESEM.

Particle Growth Experiments. Identical growth procedures were used for all three types of seed particles. In each case, the seed particles (0.200 g), DVB-55 (0.6 mL, 4 mmol), acetonitrile (29.4 mL), and AIBN (0.010 94 g, 0.0667 mmol), were placed in 30 mL wide-mouth polyethylene bottles. The reaction mixtures were vigorously agitated for several minutes in order to disperse the particles and to dissolve the initiator. The bottles were then placed in the polymerization reactor described above, using the same temperature profile. Each reaction was carried out in triplicate. Following polymerization, aliquots of the microspheres were taken from the reaction mixtures, washed with THF, and centrifuged repeatedly. These samples were used for particle size determination by Coulter multisizer and for ESEM.

Particle Size Analysis. The particle sizes and size distributions were determined using a 256-channel Coulter multisizer interfaced with a computer. A 30 μm aperture tube was chosen to accommodate the particle size range of 1−10 μm. A small sample of particles, dispersed in acetone, was added to 25 mL of Coulter Isoton II electrolyte solution and placed in an ultrasonic bath for 10 s. The Coulter multisizer measurements were confirmed using a Phillips ElectroScan 2020 environmental scanning electron microscope (ESEM).

FT-IR Analysis. Fourier transform infrared analysis was performed on a Bio-Rad FTS-40 FT-IR spectrometer. All samples were prepared as pellets using spectroscopic grade KBr in a Carver press at 15 000 psi. The spectra were scanned over the range 4000−400 cm^{-1}, in the transmission mode.

Results and Discussion

The first step in determining the particle growth mechanism was to establish whether polymerization proceeded within the continuous phase as a solution polymerization or within the precipitated polymeric phase as a micro-bulk polymerization. An autoacceleration in the reaction rate would be expected if the polymerization were to occur primarily within the polymer-rich phase.[5]

Figure 1 shows the conversion of DVB-55 to total polymer and to polymer microspheres for a polymerization carried out at 4% monomer loading in acetoni-

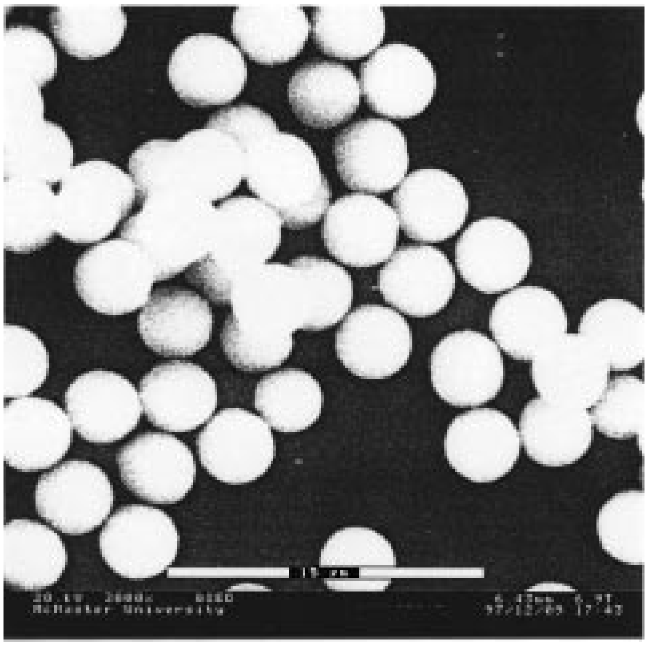


Figure 2. Scanning electron micrograph of the unmodified poly(divinylbenzene) particles used for the butylation and hydrogenation reactions.

trile. The difference between the two conversion curves reflects the presence of a soluble oligomer fraction having an apparent molecular weight of approximately 2600 g/mol, as measured by size exclusion chromatography using linear polystyrene standards.[12] An autoacceleration in the rate of monomer consumption was not observed. Instead, the conversion asymptotically approaches a plateau, characteristic of a solution polymerization where the locus of polymerization is primarily within the continuous phase and not within the precipitated polymeric phase. This is in agreement with earlier observations by Li et al.[34]

Particle Preparation. The second step was to establish how the polymer formed in the continuous phase adds to the particle surface. The key question was whether the microspheres grow by enthalpic precipitation of oligomers grown beyond their solubility limit or by entropic precipitation where oligomers captured through radical reactions desolvate upon further cross-linking to the particle surface. In the latter case, removal of the residual vinyl groups from the surface of the seed particles should prevent their growth in subsequent precipitation polymerizations.

First, a master batch of seed particles was prepared by precipitation polymerization. These particles had a number-average particle diameter, $\bar{D}_n$, of 3.8 μm and a coefficient of variation, CV, of 19%, as measured by the Coulter multisizer (Figure 2). An electron micrograph of these particles is shown in Figure 3a. This master batch was divided into three equal portions. Two of the portions were subjected to butylation or hydrogenation respectively to convert their residual surface vinyl groups into hexyl or ethyl groups.

The FT-IR spectra of the unmodified particles were measured for comparison with those for the modified particles. In the unmodified particles, the band at 2924 cm^{-1} results from the asymmetrical stretching of methylene groups while the band at 1603 cm^{-1} originates from the asymmetrical stretching of conjugated double bonds. The band at 990 cm^{-1} is associated with the CH out-of-plane deformation in monosubstituted vinyl compounds, representing residual vinyl groups.[35]

Table 1 compares the peak area ratios for the 2924, 1603, and 990 cm^{-1} bands, for all particles studied. In the case of the unmodified particles, the relative area ratios are 3.7, 7.1, and 0.51 for the 2924/1603, 2924/990, and 990 cm^{-1}/1603 cm^{-1} bands, respectively. These relative areas will be used as a baseline for comparison with the butylated and hydrogenated particles.

Seeded Polymerization Using Unmodified Seed Particles. The unmodified 3.8 μm particles were used as seeds for the preparation of larger particles by seeded precipitation polymerization. The reaction conditions were the same as those used to prepare the original particles, except for the presence of 0.2 g of seed particles having a diameter of 3.8 μm. During this growth reaction, the original seed particles increased in diameter to 4.6 μm, with a CV of 16% (Figure 3d). This particle growth was confirmed by electron microscopy (Figure 4). The two smaller particles visible in this micrograph are likely particles that were initially smaller than the 3.8 μm seed particles and as such have not grown to as large a diameter. It appears therefore that, during the polymerization in the presence of unmodified seeds, particle growth occurs exclusively on the surface of the seed particles, and secondary initiation is not observed.

The particle growth mechanism for this seeded reaction should be identical to the growth mechanism during the postnucleation stage of a nonseeded precipitation polymerization, since particle loading, reagent concentrations, and temperature all reflect those used during the initial microsphere preparation.[14]

Seeded Polymerization Using *n*-Butyl Modified Seed Particles. A sample of the unmodified 3.8 μm particles was treated with excess *n*-butyllithium to convert the residual surface vinyl groups into unreactive hexyl groups. This reaction mixture turned orange-red, due to formation of benzylic anions, and returned to white after quenching with methanol. It is expected that alkylation took place only at the surface of the particles, as diffusion of the solvated butyllithium reagent into the microspheres would be a slow process. Indeed, the butylated particles slowly decolorized bromine, likely due to reaction with residual internal vinyl groups. As well, FT-IR of the butylated particles showed only a small reduction in the level of vinyl groups. In comparison to the unmodified particles, FT-IR of the butylated particles showed an increase in the intensity of the asymmetrical methylene stretch, 2924 cm^{-1}, relative to both the asymmetrical conjugated double bond stretch, 1603 cm^{-1}, and the CH out-of-plane deformation of monosubstituted vinyl groups, 990 cm^{-1} (Table 1). These changes are in agreement with butylation of the surface vinyl groups. No change in particle diameter was observed during the butylation reaction (Figure 3b).

Subsequently, seeded precipitation polymerizations were performed using the *n*-butylated microspheres as seed particles, under reaction conditions identical to those described for the unmodified seeds. Figure 3e indicates the particle size distributions obtained after the reaction. New generations of particles have formed by extensive secondary initiation, resulting in a broad final size distribution. The electron micrograph shown in Figure 5 indicates that the new generations range in diameter from several hundred nanometers to more than 7 μm. Particles with diameters of 4 μm and larger

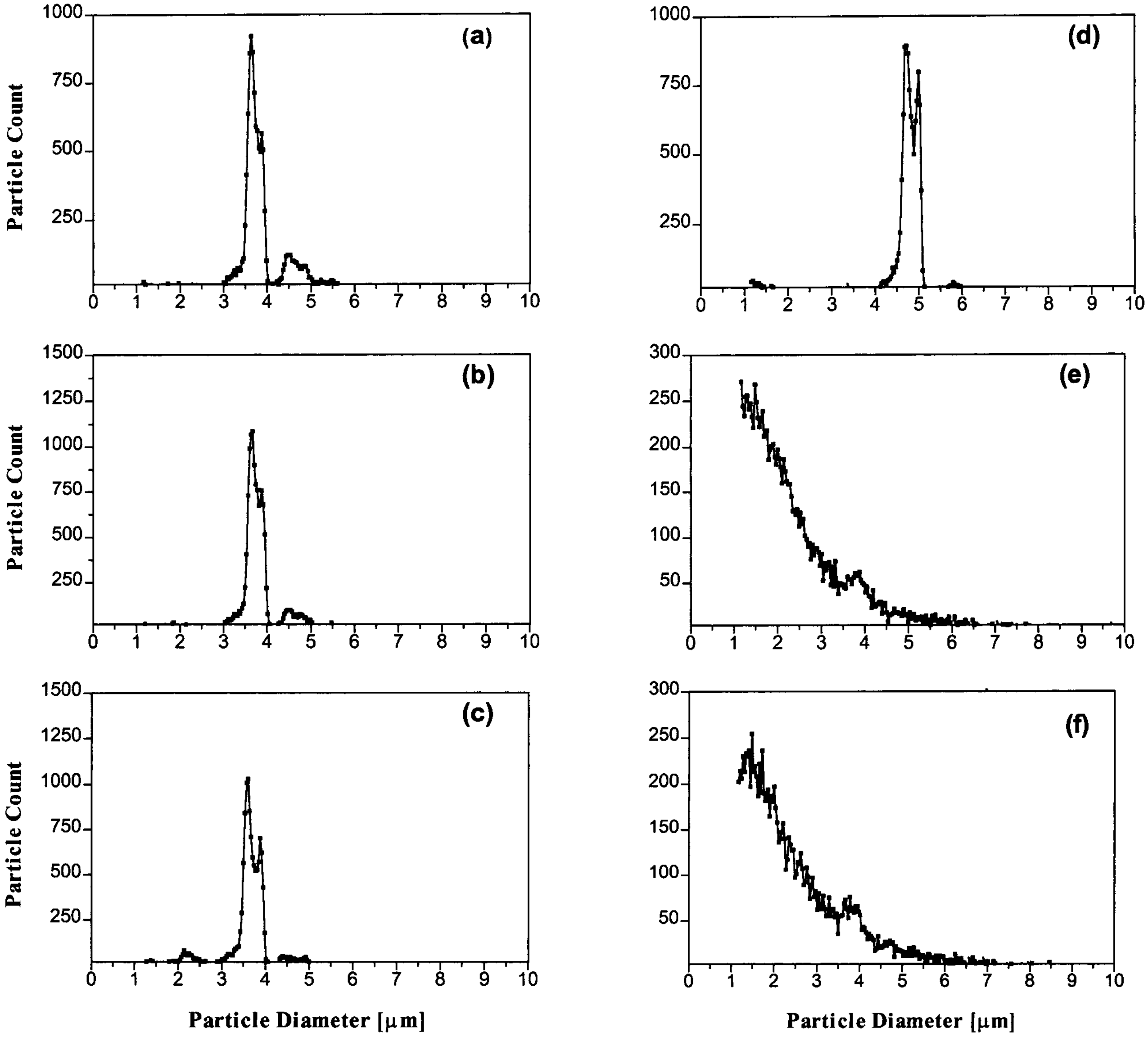


Figure 3. Particle diameters measured by Coulter multisizer analysis using a 30 μm aperture: (a) unmodified seed particles, (b) butylated seed particles, (c) hydrogenated seed particles, (d) after seeded polymerization using unmodified particles as seeds, (e) after seeded polymerization using butylated seeds, and (f) after seeded polymerization using hydrogenated seeds.

Table 1. Area Ratios of Key FT-IR Bands in the Unmodified Seed Particles, the Butylated Seed Particles, and the Hydrogenated Seed Particles

	FT-IR bands (intensity ratios)		
seed particles	2924/1603 cm^{-1}	2924/990 cm^{-1}	990/1603 cm^{-1}
unmodified	3.7	7.1	0.51
butylated	4.2	9.1	0.46
hydrogenated	4.8	10	0.48

either may be a component of the new generation or may result from the growth of some of the seed particles.

Clearly, the butylation substantially interferes with deposition of new oligomer during the seeded polymerization. It is possible that not all accessible vinyl groups were butylated, and hence some of the 3.8 μm particles could grow to diameters greater than 4 μm.

Reaction of the residual vinyl bonds with *n*-butyllithium results in the formation of pendant hexyl groups. We have found previously that aliphatic comonomers such as butyl methacrylate or dodecyl methacrylate do not interfere with particle formation and growth.[36] Nevertheless, we decided to investigate a second method of modification that would alter the particle surface to a lesser degree.

Seeded Polymerization Using Hydrogenated Seed Particles. Hydrogenating the particles was used to convert the pendant vinyl groups into ethyl groups. The DVB-55 used for the preparation of the original microspheres already contains 45% ethylvinylbenzene. Therefore, hydrogenation would be a gentle method to eliminate surface vinyl groups and to study particle growth in the absence of an entropic precipitation mechanism.

Heterogeneous hydrogenation catalysts such as platinum or palladium supported on an inert surface are commonly used for the hydrogenation of alkenes. However, a homogeneous catalyst is required for the hydrogenation of solid polymer particles. Wilkinson's catalyst, tris(triphenylphosphine)rhodium chloride, a soluble catalyst commonly used for homogeneous hydrogenations,[33] should be well-suited to the reduction of vinyl groups on a particulate surface. The hydrogenation reaction was followed by FT-IR, and the relative areas of the key bands are shown in Table 1. The asymmetrical meth-

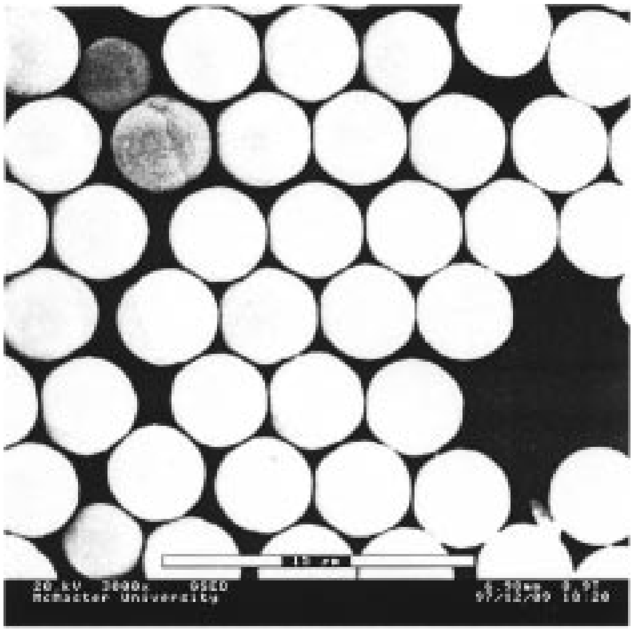


Figure 4. Scanning electron micrograph of the microspheres produced when unmodified particles were used during seeded polymerization.

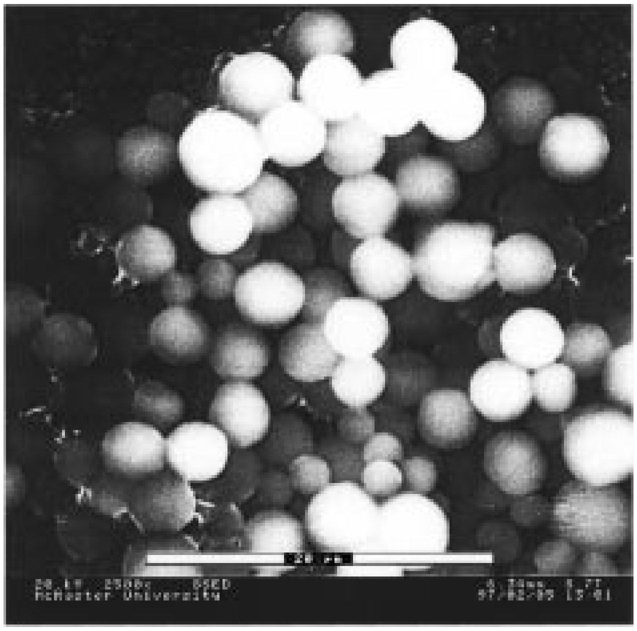


Figure 5. Scanning electron micrograph of the microspheres produced when butylated particles were used during seeded polymerization.

ylene stretch, 2924 cm^{-1}, increased with respect to the asymmetrical conjugated double bond stretch, 1603 cm^{-1}, and to the CH out-of-plane deformation of monosubstituted vinyl groups, 990 cm^{-1}. These changes are consistent with reduction of some of the vinyl groups at the surface. The particles did not change in size as a result of the hydrogenation reaction (Figure 3c).

Subsequently, a seeded polymerization was conducted using the hydrogenated microspheres as seed particles. Again, these particles easily dispersed in acetonitrile. The size and size distribution of the particles isolated from this seeded polymerization are shown in Figure 3f. As in the case of the butylated seed particles, the electron micrograph shown in Figure 6 indicates that new generations of particles had formed, with diameters ranging from several hundred nanometers to more than 7 μm. A band between 3 and 4 μm that remains visible in the final particle size plot corresponds to the original seed microspheres. These observations are consistent with the results of the polymerization using the butylated seed particles.

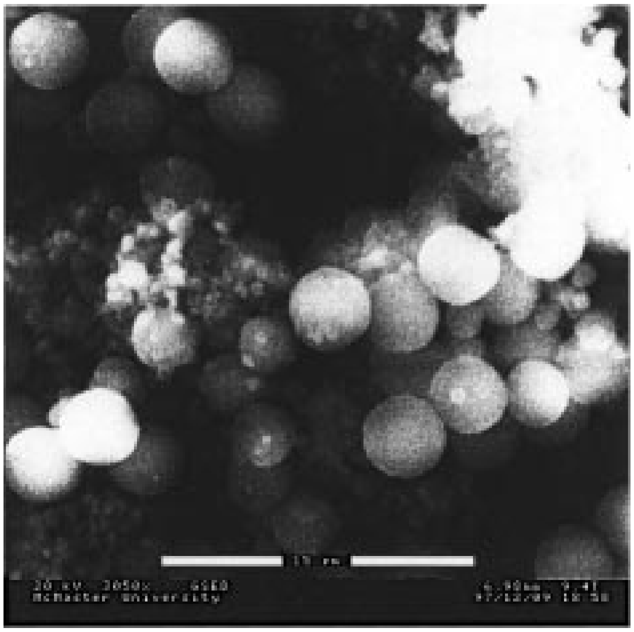


Figure 6. Scanning electron micrograph of the microspheres produced when hydrogenated particles were used during seeded polymerization.

Interpretation of Growth Mechanism. Scheme 1 outlines our investigation of the particle formation process. It includes the particle surface modifications and subsequent reactions designed to test the growth hypothesis.

Our hypothesis for the particle formation consists of two stages: nucleation and growth. Nucleation likely starts by aggregation of soluble oligomers to form swollen microgels, which subsequently desolvate to form the particle nuclei. This stage of the particle formation is outlined only briefly here as it is part of a subsequent study.

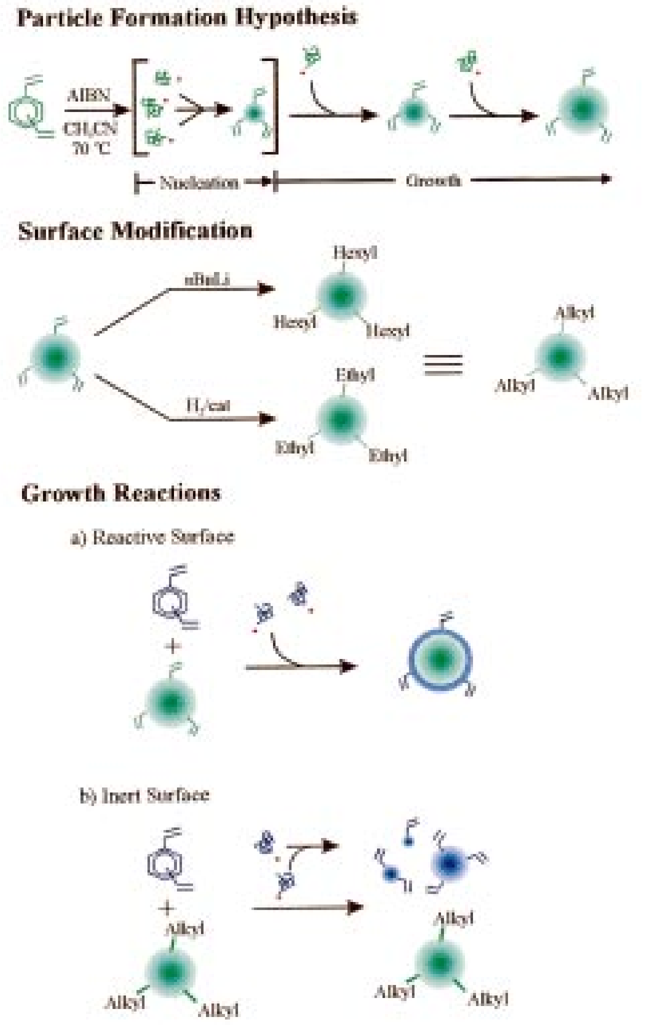
Our particle growth hypothesis is that, throughout the polymerization, soluble oligomer radicals are captured from solution by the vinyl groups on the particle surface. In particular, we propose a reactive, entropic capture mechanism, as opposed to one that is solely driven by enthalpic desolvation and deposition of the forming polymer onto the particle surface.

This hypothesis implies that the captured oligomers form the new particle surface, and hence even the final particles should contain surface vinyl groups. This allows us to test the overall hypothesis, by removing the vinyl groups from the surface of model seed particles and comparing their ability to grow during subsequent polymerizations, with that of unmodified particles.

To this end, we first prepared a master batch of seed particles by precipitation polymerization of DVB-55. This batch of particles was then divided into three parts, two of which were modified by reaction with *n*-butyllithium and by hydrogenation in the presence of Wilkinson's catalyst, respectively (surface modification).

In subsequent identical growth reactions, only the unmodified particles, containing reactive surface vinyl

Scheme 1. Proposed Particle Formation Process[a]



[a] The process has two stages. Nucleation proceeds through aggregation of soluble oligomers to form swollen microgels which internally desolvate to produce colloidally stable particle nuclei. The growth stage involves the reactive or entropic capture of soluble oligomers by surface vinyl groups, followed by desolvation. In order to test this growth hypothesis, the surface vinyl groups on a master batch of seed particles were converted to inert alkyl groups by two methods: (i) by alkylation using an excess of *n*-buLi in a mixture of 90% toluene and 10% THF; (ii) by hydrogenation using H_2 in the presence of Wilkinson's catalyst. In the subsequent seeded growth reactions involving DVB and AIBN in acetonitrile, only the reactive seed particles grew uniformly, by capturing oligomers (a). Under the same conditions, the modified, inert seed particles did not grow. Rather, in these reactions the oligomers formed, aggregated into polydisperse secondary particles (b).

groups, grew to larger diameters in a uniform fashion, without secondary particle initiation.

In contrast, neither the butylated nor the hydrogenated microspheres were able to grow, since their unreactive surfaces prevented oligomer capture. Instead, extended secondary nucleation was observed in their presence, leading to the broad final size distributions indicated in Scheme 1. This finding indicates that the presence of surface vinyl groups is essential for particle growth in this process and supports our hypothesis that particle growth is an entropic precipitation driven by radical reactions. In effect, the poly(divinylbenzene) particles do not merely provide an inert surface onto which oligomers, grown above their solubility limit, deposit by desolvation. Rather, they act as macromonomers during particle growth.

We are not certain why the secondary particles formed in the presence of the inert particles have a wide size distribution. Conducting the equivalent polymerization in the absence of any seed particles normally produces microspheres with narrow size distributions. It is likely, though, that the inert seed particles interfere with oligomer capture by the new generation of particles and thus promote continuing secondary initiation.

The oligomers involved in particle growth probably resemble the soluble polymer fraction having an apparent number-average molecular weight of 2600 g/mol that was isolated at the end of the polymerizations. These oligomers correspond to the low molecular weight fraction of the branched polymers formed by polymerization of DVB in benzene.[22]

The growth reaction involving the unmodified seed particles produces a core−shell morphology. In the present case, the core and shell both consist of DVB-55, and the experiment serves primarily as a control experiment. In an upcoming paper we will describe the formation of core−shell particles having functional shells.[37]

Implications for Particle Stabilization. As a consequence of the particle growth mechanism described above, the surface of the microspheres continuously captures soluble or highly swollen oligomers from the reaction medium. Accordingly, the particle surface at any instant during the polymerization must be a solvent-swollen, partially cross-linked gel layer. Considering the narrow particle size distribution observed despite the absence of any added steric or ionic stabilizers, we propose that this surface gel layer sterically stabilizes the particles, preventing homocoagulation that would otherwise lead to broad size distributions.

Polymer colloids, stabilized only by solvent swollen surfaces, have been known for some time. An early example are the solvent swollen microgels first prepared by Staudinger and Huseman[38]and more recently studied by Funke,[25] Burchard,[39] and Antonietti.[22] These microgels are formed by polymerizing cross-linking monomers at low monomer loadings or low conversions in good solvents.

During precipitation polymerizations carried out in a marginal, near-Θ solvent such as acetonitrile, the transient gel layer on the particle surface continuously desolvates and collapses, even while newly formed oligomer is captured.[11,12] This desolvation likely occurs by a spinodal decomposition that is both driven and frozen by cross-linking, similar to the analogous process discussed by Antonietti for small polymer microgels.[23] It can be described as a polymerization-induced phase separation (PIPS)[40] taking place first within the initially formed gel particles and subsequently within the transient gel layer on the surface of the growing microspheres.

Related surface-swollen polymer particles have been prepared earlier by a very different approach. Fitch has reviewed highly cross-linked organosols originally prepared by precipitation polymerization in poor solvent and subsequently transferred to a good solvent that swells the outer surface to the limit allowed by the cross-linking. The solvent-swollen surface gel layer obtained by this approach stabilized these organosols against aggregation.[19]

Graham and Mao have used the term auto-steric stabilization to describe the mechanism by which their polyurethane microgels avoid aggregation. Here, hydroxy-terminated poly(ethylene glycol) chains added to the polymerization are anchored on the surface of the microgels and provide steric stabilization.[41]

Naka and Yamamoto have studied the precipitation polymerization of DEGMA in the presence of good solvents that are capable of swelling the outer surface of the microspheres. Presumably, these particles are also auto-sterically stabilized by solvated polymer chains and gel anchored to the surface of the microspheres.[42]

Therefore, the monodisperse microspheres prepared by precipitation polymerization of divinylbenzene in acetonitrile could be called the following: a one-step organosol preparation, where the surface-swollen particles are prepared in situ; a polymer microgel with internal desolvation; or preferably a precipitation polymer particle auto-sterically stabilized during growth by the transient gel layer on its surface.

Conclusions

Our experimental results indicate that particle growth during precipitation polymerization of divinylbenzene in acetonitrile occurs by an entropic precipitation mechanism where soluble oligomeric species are captured from solution by reaction with vinyl groups on the particle surface. This is in contrast to the enthalpic precipitation mechanism commonly observed for dispersion polymerization, where polymer grown above its solubility limit phase separates from solution and deposits onto the surface of existing particles.

Continuous capture of oligomeric species from solution suggests that the particle surface is swollen with solvent. This transient surface gel layer stabilizes the particles during their growth stage, by a process termed auto-steric stabilization. Thus, narrow particle size distributions, similar to those obtained in dispersion polymerizations, can be achieved by precipitation polymerization in the absence of added stabilizers.

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