Synthesis of Monodisperse Emulsion-Templated Polymer Beads by Oil-in-Water-in-Oil (O/W/O) Sedimentation Polymerization

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Emulsion templating is a versatile method for the preparation of highly porous organic polymers,[1−6] inorganic materials,[7−11] and inorganic−organic composites.[12] In general, the technique involves forming a high internal phase emulsion (HIPE) (>74.05% v/v internal droplet phase) and locking in the structure of the continuous phase, usually by reaction-induced phase separation (e.g., sol−gel chemistry, free-radical polymerization). Subsequent removal of the internal phase (i.e., the emulsion droplets) gives rise to a porous replica of the emulsion. A number of research groups have investigated the synthesis of highly porous, emulsion-templated organic polymers or "polyHIPEs".[1−6] PolyHIPE materials are characterized by low-density, open-cellular structures and have found applications as separation media,[13] ion-exchange resins,[14] supports for heterogeneous catalysis,[15] polymer-supported reagents,[16] and potential tissue engineering scaffolds.[17] Thus far, most polyHIPEs have been formed by polymerization of water-in-oil (W/O) HIPEs using mixtures of styrene and divinylbenzene as the continuous phase. The polyHIPEs are produced as monolith blocks that conform to the dimensions of the reaction vessel (i.e., the

materials are "molded"). It is relatively difficult to remove the internal emulsion droplet phase from these large continuous objects. Recently, we developed a new approach that involves templating supercritical fluid emulsions.[18] This technique allows the synthesis of monolithic polyHIPEs from high internal phase CO_2-in-water (C/W) emulsions without the use of any volatile organic solvents. Moreover, removal of the droplet phase is simple because the CO_2 reverts to the gaseous state upon depressurization.

Nonetheless, in addition to problems associated with solvent removal, monolithic polymer morphologies are only appropriate for certain applications. The avoidance of shrinkage during polymerization, the development of adequate mechanical stability, or the need to use "split and mix" techniques in synthesis can all present a barrier to the use of monoliths. PolyHIPE materials can be reduced to particulate form (e.g., for use as chromatography packings) by grinding, but this can waste large quantities of the material and leads to particles with very irregular shapes and sizes. We have addressed this problem by developing a new technique for the preparation of emulsion-templated polymers in the form of monodisperse beads.

Our procedure for producing polyHIPE beads is based on the method of sedimentation polymerization, as proposed by Ruckenstein and co-workers.[19,20] In this process, individual droplets of monomer solution are partially polymerized during sedimentation through an immiscible sedimentation medium. In contrast to the more conventional technique of suspension polymerization,[21−24] the size distribution of beads produced by sedimentation polymerization may be narrow (<10% standard deviation) because the droplets are spatially isolated from one another during sedimentation. As such, droplet collision and exchange does not occur.

First, an oil-in-water (O/W) HIPE was formed by slowly adding light mineral oil (LMO, $\rho = 0.838$ g/cm^3) to an aqueous solution of monomers while stirring. We chose acrylamide (AM) and *N,N*-methylenebisacrylamide (MBAM, 20% w/w cross-linker based on AM) since these monomers are known to polymerize rapidly under sedimentation polymerization conditions when ammonium persulfate is used as the initiator.[19,20] The ratio of the oil phase to the water phase was 8:2 v/v. In the presence of a suitable surfactant system (e.g., sodium dodecyl sulfate, SDS + poly(vinyl alcohol), PVA), a stable O/W HIPE was formed. This HIPE was then injected into a glass column containing a heated sedimentation medium (mineral oil) using a syringe pump.[25]

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Table 1. Reaction Conditions for Preparation of Emulsion-Templated Beads[a]

sample	monomer	T (°C)	surfactant[b]	internal oil phase[c]	sedimentation medium (LMO:HMO v/v)[d]	concentration of TMEDA in a sedimentation medium (left) + internal oil phase (right) (% v/v)[e]	
1	AM	90	SDS	LMO	1:0	0	0
2	AM	60	SDS	LMO	2:8	2.4	0.088
3	AM	60	Triton	LMO	2:8	2.4	0.066
4	AM	60	Triton	CH/LMO (75:25)	1:0	15	0.066
5	AM	60	Triton	LMO	2:8	3.6	0.070
6	AM	60	Triton	CH/LMO (44:56)	1:0	15	0.066
7	AM	60	Triton	CH/LMO (37:63)	1:0	15	0.066
8	NIPAM	60	Triton	LMO	2:8	3.6	0.13
9	HEMA	90	Triton	LMO	0:1	12	0.13
10	AA	70	Triton	CH/LMO (37:63)	1:0	15	1.6

[a] Typical conditons: (1) Aqueous monomer/surfactant/initiator solution prepared from acrylamide (AM, 15.33 g), *N,N*-methylene bisacrylamide (MBAM, 3.106 g), distilled water (40 cm³), and poly(vinyl alcohol) (PVA, 10 000 g/mol, 80% hydrolyzed, 2.25 g). (2) HIPE prepared mixing monomer solution (3.0 cm³) with surfactant {SDS (0.7 g) or Triton X-405 (0.49 g)}, ammonium persulfate (APS, 0.030 g), and an internal oil phase to give an overall O/W phase volume of 8:2 (see Supporting Information for specific monomer solution compositions). [b] SDS = sodium dodecyl sulfate; Triton = Triton X-405 = polyoxyethylene isooctylcyclohexyl ether. [c] LMO = light mineral oil (ρ = 0.838 g/cm³); CH = cyclohexane (ρ = 0.779 g/cm³); volumetric ratios in parentheses. [d] HMO = heavy mineral oil (ρ = 0.862 g/cm³). [e] TMEDA = *N,N,N,N*-tetramethylethylenediamine (ρ = 0.770 g/cm³).

Table 2. Physical Characterization Data for Emulsion-Templated Beads

sample	intrusion volume[a] (cm³/g)	bulk density[b] (g/cm³)	average pore size[a,c] (μm)	specific surface area[d] (m²/g)	mean bead diameter[e] (mm)	standard deviation in bead diameter (%)[e]
1	0.93	0.479	2.18 (98.0), 0.10 (2.0)	6.0	1.52	5.3
2	2.82	0.166	2.47 (99.8), 0.06 (0.2)	17.1	2.17[f]	6.3[f]
3	3.29	0.159	8.67 (64.8), 4.83 (35.2)	3.5	2.11	7.6
4	5.09	0.130	8.79 (62.8), 4.80 (36.7), 0.24 (0.5)	9.8	2.16	2.6
5	7.29	0.091	11.72 (99.7), 0.28 (0.3)	10.8	2.25	3.7
6	5.07	0.132	8.36 (59.2), 5.61 (40.5), 0.26 (0.3)	7.5	1.99	4.1
7	5.84	0.122	12.62 (93.4), 5.19 (6.3), 0.46 (0.3)	5.0	1.85[f]	6.3[f]
8	8.09	0.092	10.21 (100)	19.8	1.91	7.8
9	1.23	0.329	4.89 (100)	2.2	1.53[f]	4.9[f]
10	0.88	0.502	8.76 (65.1), 5.37 (34.9)	0.7	1.64	10.3

[a] Measured by mercury intrusion porosimetry over the pore size range 7 nm to 200 μm. [b] Estimated from weighing n beads ($n \approx 20$) and dividing by the volume of the beads, v, i.e., $v = n \times 4/3\pi r^3$ (where r = average bead radius). [c] Value in parentheses is the percentage of the total pore volume accounted for by each pore size, calculated from plot of log(differential intrusion volume) vs pore diameter. [d] Measured by N₂ adsorption−desorption using the Brunauer−Emmett−Teller (BET) method. [e] Calculated by measuring >100 bead diameters. [f] Some bead agglomeration was observed.

Individual droplets of O/W HIPE were formed with a diameter of ≈2 mm. The droplets sank slowly through the sedimentation medium and were collected at the bottom of the glass column as partially polymerized spherical beads. After injection and sedimentation, the beads were left in the heated sedimentation column for an additional 3 h to complete the polymerization. At the end of the reaction, the beads were recovered by filtration, washed with *n*-hexane and acetone, and then dried under vacuum at 50 °C.

A series of beaded polymer samples was prepared by this method under reaction conditions outlined in Table 1. The physical properties of these materials are summarized in Table 2. One practical difficulty associated with the technique of sedimentation polymerization is that partial gelation must occur rapidly (usually within a few seconds) such that the droplets do not coalesce at the bottom of the sedimentation column.[19,20] This requirement is even more stringent in our new system because the polymer phase (which gives rise to mechanical stability) constitutes only a small fraction of the total droplet volume (<20% v/v). One method to accelerate gelation is to carry out the reaction at elevated temperatures. When the sedimentation medium was heated to 90 °C (sample 1), uniform spherical beads could be formed with a relatively narrow size distribution (5.3%). The intrusion volume for sample 1 was low (0.93 cm³/g) in comparison to other polyHIPE systems,[1–6]

and the bulk density was correspondingly high (0.479 g/cm³). Analysis of the beads by electron microscopy showed that some of the emulsion structure had been templated, but that there had also been significant emulsion collapse prior to gelation. This led to a relatively dense, partially porous structure. The instability of the emulsion can be rationalized by the fact that the system is heated from ambient temperature to 90 °C within a few seconds. Attempts to counteract this instability at high temperatures (e.g., by raising the surfactant concentration) were unsuccessful.

The degree of porosity in the beads could be increased considerably by carrying out the polymerization at lower temperature (60 °C) in the presence of a redox co-initiator, *N,N,N,N*-tetramethylethylenediamine (TMEDA).[26,27] Low-density porous structures were obtained when a small quantity of TMEDA was added to both the sedimentation medium and to the internal oil phase of the emulsion (sample 2). TMEDA was not added directly to the aqueous phase (although TMEDA is significantly water soluble) to prevent rapid gelation prior to injection. Slightly higher intrusion volumes were observed when a nonionic surfactant, Triton X-405, was used in place of SDS (sample 3). The intrusion

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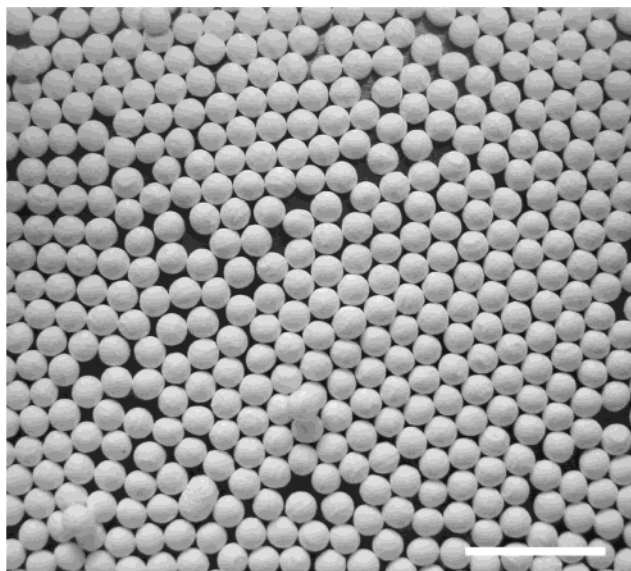*Chem. Mater., Vol. 14, No. 10, 2002* **4019**

Figure 1. Optical image of emulsion-templated beads (sample 4, scale bar = 10 mm). Average bead diameter = 2.16 mm. Standard deviation in bead diameter = 2.6% (56 μm).

Figure 2. Electron micrographs of individual emulsion-templated beads (sample 4). (a) Whole bead (scale bar = 500 μm). (b) Sectioned "half-bead" showing internal pore structure (scale bar = 500 μm). (c) Magnified image of bead surface showing pore structure (scale bar = 100 μm). (d) Magnified image of a fracture surface in a sectioned bead showing internal pore structure (scale bar = 100 μm).

volumes for samples 2 and 3 were $\approx$3 times greater than that observed for sample 1. Electron microscopy showed that most of the original emulsion structure was retained in these materials.

It was found that the degree of porosity could be increased by raising the concentration of TMEDA in the sedimentation medium (samples 4–7) and by substituting the internal LMO phase with a less viscous mixture of cyclohexane and LMO (samples 4, 6 + 7). In addition to increasing porosity, these conditions also led to uniform, unagglomerated spherical beads. Figure 1 shows an optical image of sample 4. The beads are essentially monodisperse with an average diameter of 2.16 mm and a size distribution of just 2.6%. Figure 2 shows a series of electron micrographs for individual beads taken from sample 4. It can be seen that the internal structure is uniformly porous and consists of a "skeletal replica" of the original O/W HIPE. The pore structure is highly interconnected and there are open pores on the bead surface that are connected to the bead interior (see Figure 2c). The size of the macropores was found to be in the range 2–15 μm. The pore size distribution was often bimodal in these materials (see Table 2).[25] BET surface areas were relatively low (<20 m^2/g) in all of these samples, suggesting that there was little (if any) micro- or mesoporosity in the walls of the templated polymer structures. This suggests that the removal of water during drying did not give rise to any permanent porosity that persisted in the dry state (i.e., all of the porosity in the samples arose from templating rather than from porogen effects). A similar observation was made in the case of emulsion-templated AM/MBAM copolymers synthesized from C/W HIPEs.[18] Macroporous polyHIPE structures were also observed when lower cross-linking levels were employed (sample 6 and sample 7, 10 and 1% w/w MBAM, respectively), although some agglomeration between beads was observed at the lowest cross-linking level (sample 7).[25] We have carried out preliminary experiments with vinyl monomers other than AM and have found that these too can be polymerized to form well-defined polyHIPE beads. For ex-
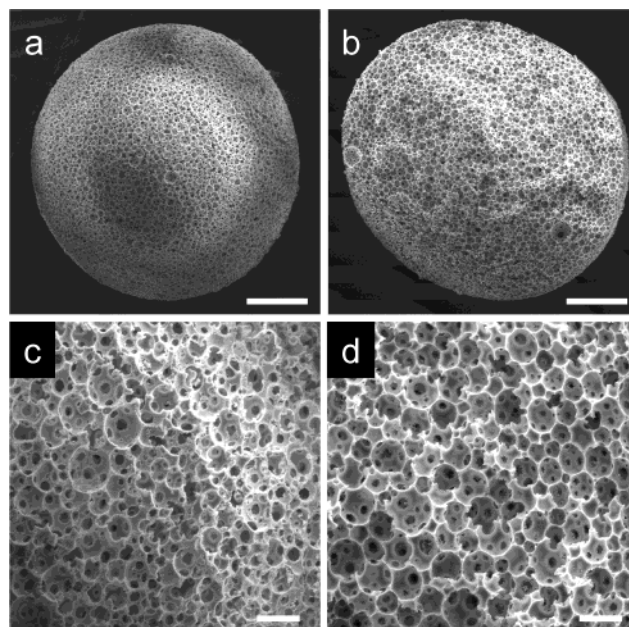
ample, the sedimentation polymerization of O/W HIPEs containing *N*-isopropylacrylamide (NIPAM, sample 8) led to very porous beads (intrusion volume = 8.09 cm^3/g, bulk density = 0.092 g/cm^3). Less reactive monomers such as hydroxyethyl acrylate (HEMA, sample 9) were also compatible with this methodology but intrusion volumes were lower (<1.5 cm^3/g) and bulk densities were relatively high (>0.3 g/cm^3), even when elevated temperatures and high TMEDA concentrations were employed. Similarly, materials based on acrylic acid (AA, sample 10) exhibited moderate degrees of porosity and partially templated pore structures.

It should be noted that our materials differ from macroporous beads produced by suspension polymerization[21–24] in three important ways. First, intrusion volumes are much higher, reaching values of greater than 8 cm^3/g. Second, the pores in these materials are considerably larger (2–15 μm) than the size range that is readily obtained in macroporous systems.[28] Third, the beads are produced in a monodisperse form with size distributions as low as 2%.

Porous, hydrophilic polymers are useful in a wide variety of applications such as chromatography, catalysis, drug delivery, and tissue engineering. Our new methodology allows the synthesis of emulsion-templated polyacrylates in the form of monodisperse spherical beads. We view the development of beaded materials with large macropores (2–15 μm) and high pore volumes as particularly useful in conjunction with systems where mass transport would be impeded by smaller diameter pores (e.g., macromolecules, large biomolecules, and viscous solutions). Future work will focus on such applications and on the extension of this approach to a wider range of organic and organic–inorganic composite

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systems. The synthesis by this method of emulsion-templated silica beads with hierarchical mesoporous/macroporous structures will be the subject of a future report.

Supporting Information Available: Full experimental details, monomer solution compositions, optical images, electron micrographs, and mercury intrusion porosimetry analysis (PDF). This information is available free of charge via the Internet at http://pubs.acs.org.

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