

Table **I1**

^aThis measurement has been obtained with a polypropylene sample containing 0.4% of SA residues, using the same experimental conditions adopted for PsBPP-g-SA copolymers.

copolymers influences not only the chemical reactivity of these materials but also the surface properties of the metal-polymer interfaces in the melt state.

For this reason, adhesion properties of PsBPP itself and PsBPP-g-SA polymers, containing variable amounts of grafted SA residues, were investigated on the surface of aluminum foils. The obtained **results** are reported in Table 11. As can be seen from this table, adhesion strength increases with the increase of the SA content in the PsBPP-g-SA polymers, suggesting the presence of chemical reactions between melt-grafted PsBPP-g-SA and the aluminum surface.

According to the adhesion mechanism suggested for

polyolefins grafted with MA,⁴⁰ the enhancement of the peel energy for PsBPP has to be attributed to chemical reactions occurring between the anhydride moieties in the melt polymers and the hydroxyl groups always present in the aluminum oxide layer covering the metal surface. $40-42$

It may be observed, moreover, that the highest adhesion strength for PsBPP-g-SA polymers was obtained when the SA content in this material was **2.4%;** the obtained value of **2153** N/m is of the same order of magnitude **as** the value obtained for the PP-g-SA sample containing **0.4%** grafted SA residues **(3537** N/m in the reference experiment 6 in the Table 11). This behavior has been ascribed to the very different bulk viscoelastic properties of PsBPP-g-SA rubber in comparison with the PP-g-SA, which possesses a pronounced crystallinity, probably due to the induction of a highly crystalline surface layer (e.g., transcrystalline). 42

Acknowledgment. We are indebted to the "Progetto Finalizzato Chimica Fine e Secondaria 11" of the Consiglio Nazionale delle Ricerche for financial support.

Registry No. Bp, 94-36-0; Al, 7429-90-5.

(41) Ulren, L.; Hjertberg, T. J. *Appl.* **Polym. Sci. 1989, 37, 1269. (42) Schonhorn, H. Macromolecules 1968,1, 145.**

Concentrated Emulsion Polymerization Pathway to Hydrophobic and Hydrophilic Microsponge Molecular Reservoirs

E. Ruckenstein* and **L. Hong**

Department of Chemical Engineering, State University of New York at Buffalo, Buffalo, New York 14260

Received March 13, 1992. Revised Manuscript Received July 13, 1992

Porous particles of micrometer size have been prepared using the concentrated emulsion polymerization method. The dispersed phase with a volume fraction greater than **0.74,** contained a monomer, or a polymer, of a surfactant when the monomer of the dispersed phase was hydrophobic, and a surfactant solution in a hydrocarbon liquid when the dispersed phase was hydrophilic. **Four** kinds of porous materials have been achieved: (1) hydrophobic cross-linked (with divinylbenzene (DVB) as the cross-linking agent) polystyrene particles; (2) hydrophilic cross-linked polyacrylamide (with methylenebisacrylamide **(MBAA) as** the cross-linking agent) particles; (3) hydrophobic porous nutshells of cross-linked polystyrene surrounding a void filled with sparse poly(vinylbenzy1 chloride) (poly (VBC)); **(4)** hydrophilic nutshells of cross-linked polyacrylamide encapsulating loosely entangled poly(ethy1ene oxide) (poly (EO)) **coils.** The nutshell structure was obtained by using a two-step procedure: First, a concentrated emulsion of oil in water (o/w) with a dispersed phase consisting of monomers (VBC and **DVB)** dissolved in a porogen was polymerized, or dissolved in water was prepared. In the second step, styrene/DVB was introduced into the o/w emulsion and an aqueous solution of acrylamide/MBAA into the w/o emulsion. The resulted systems were allowed to polymerize, thus generating polymer shells encapsulating either sparse poly(VBC) matrixes or loosely to polymerize, thus generating polymer shells encapsulating either sparse poly(VBC) matrixes or loosely entangled poly(E0). The porous hydrophobic polymeric beads of the fit kind have relatively *small* surface areas of **20-40** m2/g, while those of the third kind have surface areas of about **300** m2/g. The cross-linked particles of polyacrylamide of the second kind prepared with water **as** the porogen adsorb 68 mg of enzyme lipase per gram of polymer. The polyWC) encapsulated in the porous nutshell particles was functionalized with anchoring quaternary phosphonium cations. This functionalized substrate possesses a high adsorption capacity for cobalt carbonyl anions $(2.78 \text{ mmol of Co/g of polymer})$ via ion pair formation as well as via capacity for cobalt carbonyl anions $(2.78 \text{ mmol of Co/g of polymer})$ via ion pair formation as well as via physical adsorption.

Introduction

Porous polymer particles are used in many applications, such **as** chromatography, ion exchange, reactive polymer matrixes, and more recently in controlled release of drugs.¹

The synthesis of these macroreticular particles is, in general, **based** on the suspension polymerization of a dispersed phase that consists of a monomer, a cross-linking agent,

^{*} To **whom correspondence should be addressed.**

⁽¹⁾ Eury, **R.; Patel, R.; Longe, K.; Cheng, T.; Nacht, S. Chemtech 1992, Jan, 42.**

Microsponge Molecular Reservoirs

an initiator, and a suitable inert solvent that functions **as** porogen.² The size of the particles depends on the suspending medium as well as on the nature and amount of dispersant it contains. The porosity of the particles is controlled by varying the volume fraction of the porogen and by adjusting the concentration of the cross-linking agent.3

In the present paper a novel method for the preparation of porous polymer particles which is based on the polymerization of concentrated emulsions⁴ is proposed. The concentrated emulsion is obtained by dispersing with stirring a hydrophobic (hydrophilic) liquid into a surfactant-containing hydrophilic (hydrophobic) liquid. The volume fraction of the dispersed phase is larger than **0.74,** which represents the volume fraction of the most compact arrangement of spheres of equal radii and can be as large **as 0.99.** The concentrated emulsions have the appearence and behavior of gels and, for this reason, can be easily handled.⁵ The concentrated emulsion is stabilized by the adsorption of the surfactant on the surface of the dispersed droplets. In contrast to suspension polymerization, the concentrated emulsion method employs a small volume fraction of continuous phase, and this offers some advantages, such as easier surface modifications⁶ and, as demonstrated below, the generation of nutshell particles.

Four kinds of polymeric beads have been prepared: (1) porous highly cross-linked hydrophobic polystyrene particles; **(2)** lightly cross-linked hydrophilic polyacrylamide particles; (3) porous nutshells of highly cross-linked polystyrene encapsulating sparse poly(VBC) matrixes; **(4)** hydrophilic particles with lightly cross-linked polyacrylamide nutshell encapsulating loosely entangled poly(E0) molecules. All four kinds of particles can constitute reservoirs for chemically active species and medicines. As examplea, such particles are used for trapping cobalt carbonyl complexes or immobilizing the enzyme lipase.

Experimental Section

Reagents Used. Styrene (Aldrich, 99%), divinylbenzene (Aldrich, tech., 55%), acrylic acid (Aldrich, 99%)) and vinylbemy1 chloride (Kodak, p and m isomeric mixture) were distilled under vacuum before use. Acrylamide (Aldrich, 99%), tributylphosphine (Aldrich, 92%)) cobalt carbonyl (Fluka, purum 90-95%), poly- (ethylene oxide) (Aldrich, 99%) *A4* = 600000), sodium dodecyl sulfate (SDS, Aldrich, 99%), sorbitan monooleate (Span-80, Fluka), **NJV-methylenebisacrylamide** (MBAA, Aldrich, 99%), Lipase (Sigma, EC3.1.1.3., Type VII, 900 units/mg solid), and solvents were used without further purification. The aqueous solution of sodium acrylate (1.81 M, $pH = 7.20$) was prepared by neutralizing the acrylic acid with a solution of sodium hydroxide.

Instruments Employed. Energy-dispersive spectroscopy surface analysis (EDS) was performed on a PGT/IMIX field emission electron microscopy equipment (15 keV). Porous polymer particles were investigated with scanning electron microscopy (SEM, Hitachi S-800). The specific surface area and the pore size distribution were measured with a physical adsorption analyzer (Accusorb 2100E, Micromeritics). The infrared absorption spectrum of the encapsulated cobalt carbonyl anions was **obtained** with a Mattaon Alpha Centauri FT-IR instrument. The elemental analyses for C1, P, and Co were carried out by Quantitative Technologies, Inc. (Bound Brook, NJ).

Measurement of the Specific Surface Area and Pore Size Distribution. The polymer samples (the weighta used have been

in the range 0.02-0.2 g) were first degassed at room temperature overnight under $1-5 \mu mHg$ and then at 75-80 °C for 2 h under the same pressure. To estimate the error of the instrument, a silica catalyst support (Aldrich, $S_w = 600 \text{ m}^2/\text{g}$) was employed to measure the surface area and a value of $430 \text{ m}^2/\text{g}$ was obtained. As for the estimation of the pore size distribution, our instrument has allowed us to determine only pore sizes smaller than 50 **A.** However, larger pores of submicron sizes could be measured from the SEM pictures.

Preparation of **Porous Particles by Concentrated Emulsion Polymerization Method. An** aqueous solution of 0.5 g of SDS in 4 mL of water was prepared in a 150-mL round-bottom flask. Then a mixture containing 1.5 mL of DVB, 2 mL of styrene, 12.5 mL of toluene (or decane), and 25 mg of azobisisobutyronitrile (AIBN) **as** initiator was introduced dropwise, under stirring with a Teflon blade (about 600 rmp), over about 20 min, at room temperature. The obtained concentrated emulsions were sealed in glass tubes and polymerized at 40 "C for 3 days. The porogen and unreacted monomer were removed from the porous polymer particles by extraction with methanol in a Soxhlet funnel for 24 h. Finally, the particles were vacuum dried.

Preparation of **Hydrophobic Particles with a Porous Nutshell Structure by a Two-step Concentrated Emulsion Polymerization Method.** A solution containing 0.5 g of SDS in 4 mL of water was introduced into a 150-mL round-bottom flask. Then a solution of **VBC** (1 g, 6.65 mmol) in 13 mL of toluene-decane mixture (volume ratio $= 1/1$) containing 26 mg of AIBN was added dropwise, under stirring with a Teflon blade (about 600 rpm), over about 20 min, at room temperature. The resultant gellike concentrated emulsion (with a volume fraction of the dispersed organic phase of 0.78) was polymerized at 40 "C for 16 h. After polymerization, the concentrated emulsion was cooled to room temperature, and DVB (3.5 mL) was added slowly under vigorous stirring (about 700 rpm). The emulsions loaded with DVB were packed tightly by shaking, sealed in glass tubes, and polymerized for 48 h at 40-45 °C. The aggregates of fine particles of polymer thus obtained were dispersed by stirring in methanol. After filtration, the polymer powders were purified in a Soxhlet funnel with methanol for 24 h, followed by vacuum drying. The polymer particles thus obtained have a porous nutshell encapsulating a sparse matrix of poly(VBC) (see Resulta and Discussion).

Conversion of the Encapsulated Poly(VBC) into Poly- [**(vinylbenzy1)tributylphosphonium chloride] (poly(VBPC)), via Quarternization.** Tributylphosphine (2.0 g, 10 mmol) was introduced into a suspension of hydrophobic particles with porous nutshell structure (2.5 g, containing 3.7 mmol of chlorine) in 20 mL of DMF. The mixture was stirred under a N_2 atmosphere, at 60-65 "C for 72 h. After cooling, the mixture containing the quaternized polymer powder was introduced into a **60-mL** mixture of ethyl ether and petroleum ether $(V/V = 1/4)$. The filtered polymer powder was introduced into 20 **mL** of THF, precipitated with 60-80 mL of petroleum ether (this purification step was repeated three times) and finally dried under vacuum at 50 "C.

Entrapping Co(CO)₄ Anions and NaCo(CO)₄ Complexes. Dark red crystals of $Co_2(CO)_8$ (0.588 g, 1.62 mmol) were added to a suspension of polymer beads which encapsulate poly(VBPC) in a mixture of an aqueous solution of NaOH (0.5 M, 50 mL) and toluene (30 mL). This slurry was stirred at room temperature for 1.5 h and filtered in a Büchner funnel. The $Co(CO)₄$ loaded powder was then purified in a Soxhlet with CH₂Cl₂ for 24 h and finally dried under vacuum.

Preparation of **Hydrophilic Particles [Polyacrylamide and Poly(sodium acrylate)] with Water as Porogen. To** a solution of Span-80 (1.0 g) in 4 **mL** of m-xylene held in a 100-mL round-bottom flask, 20 **mL** of an aqueous solution of acrylamide $(4 g, 56 mmol)$, MBAA $(0.5 g, 3.5 mmol)$ and initiator $K_2S_2O_8(10$ mg) were added dropwise, under stirring with a Teflon blade (about 600 rpm), over about 200 min, at room temperature. The resultant gellike concentrated emulsion of water in oil (w/o, with a volume fraction of dispersed aqueous phase of 0.83) was sealed in glass tubes and polymerized at 40 "C for 3 days. To precipitate the polymer beads, the polymerized emulsion containing polyacrylamide was introduced into THF. The surfactant and the nonpolymerized monomer were removed from the polymer by extraction with THF in a Soxhlet for 4 h. The particles were

⁽²⁾ Sherrington, D. C. In *Macromolecular Syntheses;* Pearce, E. M., Ed.; Wiley: New York, 1982; Vol. 8, p 30.

^{.;} whey. New York, 1962, vol. o, p oo.
(3) Howard, G. J.; Midgley, C. A. J. Appl. Polym. Sci. 1981, 26, 3845.
(4) Ruckenstein, E.; Kim, K.-J. J. Appl. Polym. Sci. 1988, 36, 907.
(5) Ruckenstein, E.; Park, J.-S. J. Polym. S

⁽⁶⁾ Ruckenstein, E.; Hong, L. *Chem. Mater.* **1992,** *4,* **122. 1988,26, 529.**

 (a)

 (b)

Figure 1. Scanning electron micrograph of cross-linked polystyrene particles: (a) particles prepared by using toluene **as** porogen (the length of the scale is $3.7 \mu m$): (b) particles prepared by using decane as porogen (the length of the scale is $4.0 \mu m$).

finally vacuum dried. For the preparation of poly(sodium acrylate), a gellike concentrated emulsion of w/o was prepared using 20 mL of an aqueous solution of sodium acrylate $(0.17 \text{ g/mL}, \text{pH} = 8.5)$ containing 10 mg of K₂S₂O₈; the other conditions were the same **as** for polyacrylamide.

Preparatioon of **Hydrophilic Particles with Polyacrylamide Nutshell and Encapsulated Poly(ethy1ene oxide).** To a solution of Span-80 **(1.0** g) in **4** mL of decane held in a **100-mL** round-bottom flask, a solution of poly(ethylene oxide) $(0.2 g, MW = 600000)$ and $K_2S_2O_8$ $(8 mg)$ in 15 mL of water was added dropwise, under stirring (about **600** rpm), over about **20** min, at room temperature. To the gellike w/o concentrated emulsion thus obtained, an aqueous solution of acrylamide **(2 g, 28** mmol) and **MBAA (0.125** g, **1.75** mmol) in **5** mL of water was added slowly under vigorous stirring (about **700** rpm). The obtained emulsion was poured and sealed into glass tubes and subjected to polymerization at **40-45 "C** for **48** h. The aggregates of fine particles were precipitated by stirring the polymerized emulsion in THF. Further, the polymer was purified with THF in a Soxhlet for 8 h and vacuum dried.

Lipase Immobilized to the Hydrophilic Substrate. Lipase **(25** mg) were dissolved in **50** mL of a phosphate buffer solution (0.89 M, KH2P04/Na2HP04, pH = **7.0)** in a **150-mL** flask. Polyacrylamide particles **(200** mg) thus obtained were suspended into the solution by stirring at room temperature for **2** h. The system was subsequently centrifuged to precipitate the enzyme-containing substrate. The liquid was decanted and used for the determination of the enzyme which remained in the solution, on the basis of the visible absorption spectrum at **740** nm.7

Results and Discussion

Preparation of Porous Particles by the Concentrated Emulsion Polymerization Met hod. Two kinds **of** cross-linked polystyrene porous particles (with 21 mol % **DVB)** have been prepared by the concentrated emulsion polymerization method, using either toluene or decane **as** the porogen. Because toluene is a good solvent for polystyrene, while decane is a "nonsolvent", the pore mor-

Figure 2. Pore sizes (below **50 A)** distribution of cross-linked polystyrene particles prepared by using toluene **as** porogen.

phologies obtained were different (Figure 1). The particles based on toluene (with a volume fraction of dispersed phase of 78%) have very small pores which cannot be detected in the SEM picture (Figure la). The pore size distribution between **20** and **50 A** determined with the adsorption analyser is given in Figure 2. The results almost coincide with those of a previous study⁸ in which porous polystyrene beads have been prepared by suspension polymerization. In contrast, the porous particles based on decane have pore sizes as large as $0.2 - 0.3 \mu m$, which can be detected in the **SEM** pictures (Figure lb), and also larger surface areas $(47 \text{ m}^2/\text{g})$ than those based on toluene $(25 \text{ m}^2/\text{g})$. The main difference between the concentrated emulsion polymerization and the suspension polymerization consists in the much smaller volume fraction of continuous phase in the former than in the latter. The gellike emulsion that constitutes the precursor in the former case contains polyhedral cells separated by thin films of continuous phase. The polymerization of the cells does not appreciably change their size, which is in the range 0.1-10

⁽⁷⁾ Clark, J. *M. Experimental Biochemistry; W.* **H. Freeman: San**

Table I. Preparation of Porous Nutshell Particles by a Two-Step Concentrated Emulsion Procedure

	VBC-DVB		ST-DVB		elem anal. $(mmol/g \text{ of})$ polymer)	specific surface
entry	(mol % of DVB)	porogen (12.5 mL)	(mol % of DVB)	Cl		area $(m^2/g)^b$
	1.0 g-0.11 g (6.3%)	$decay$ toluene $(V/V = 1)$	1.8 g-1.4 g (21%)	1.61	0.93	225
2	as above	as above	$3.2 \text{ g}^a (55\%)$	1.49	0.83	332
3	as above	toluene alone	as above	1.54		70
4	as above	decane alone	as above	1.42		100
5	1.0 g-0.60 g (28%)	$decane/toluene (V/V = 1)$	as above	1.58		284

^a Only DVB was introduced, which contains 45 mol % of 3- or 4-ethylvinylbenzene. ^b The surface area of porous particles was measured before quaternization.

Figure 3. Schematic illustration of the process for generating porous nutshell particles: A, cell containing a nucleus; B, polymerization of styrene/DVB in the non-solvent layer; C, formation of the porous nutshell particle.

 μ m. In suspension polymerization the sizes are larger, in the range $3-300 \mu m$.¹ The fact that the volume fraction

of the continuous phase is very small in the concentrated emulsion method is particularly advantageous in the preparation of porous nutshell particles discussed in the next section.

Porous Nutshell Particles and Their Use as Hosts for Cobalt Carbonyl Anions. A two-step concentrated emulsion polymerization procedure is suggested to prepare porous nutshell particles. The detailed compositions are listed in Table I. In the first step, a gellike concentrated emulsion of a mixture of solvent/non-solvent for the polymer (as porogen), containing small **amounts** of VBC and DVB and an initiator AIBN, dispersed in water **was** prepared and polymerized at 40 °C for 16 h. In the second step, a mixture of styrene and DVB was introduced into the polymerized gellike emulsion, and the resulting system was polymerized for 3 days. During the first polymerization, the cross-linked poly(VBC) matrix is swollen by the solvent (toluene), and a nucleus is generated surrounded by a liquid layer containing the nonsolvent (decane) **as** the major ingredient. The mixture of styrene-DVB, introduced in the second step, mixes with decane but cannot penetrate into the already polymerized nucleus and then polymerizes to generate a porous nutshell of crosslinked

 (a)

Figure 4. Scanning electron micrographs of porous nutshell particles containing poly(W3C): (a) material from **1** of Table I; (b) material from **2** of Table I. The lower part of both micrographs represent a 5-fold magnification of the rectangular area marked in the upper part.

Figure 5. N₂ adsorption isotherm of porous nutshell particles at **77** K **(2** and *5* in Table I).

Figure 6. Energy-dispersive spectroscopy of porous nutshell particles containing pendant phosphonium groups (1 and **2** in Table I).

polystyrene surrounding a "void" filled with a sparse poly(VBC) matrix (this mechanism is depicted in Figure 3). Since the volume fraction of the continuous phase is small, it is easier for the mixture of styrene-DVB to surround the prepolymerized particles than when the volume fraction is large.

The SEM picture (Figure 4) shows that the nutshell resembles a shell of marblelike pieces, with submicron size pores among them. The pores are of submicrometer size, can be estimated directly from the pictures, and are a result of the non-solvent effect of decane for polystyrene. The nature of the porogen³ and the extent of crosslinking of poly(VBC) are expected to affect the structure of the nutshell particles. When a single porogen is used (3 and **4** of Table I), the porous particles have relatively low specific surface areas. When a solvent/non-solvent porogen mixture is employed, the surface area is much larger. Their effect on the surface area of the particles is presented in Table I. In addition, if the extent of cross-linking of the encapsulated poly(VBC) increases (5 of Table I), the density of the polymer particle increases, and the surface area and pore volume diminish. The comparison of N_2 adsorption volumes by the porous particles (2 and 5 of Table I; Figure **5)** is in agreement with this conclusion.

The EDS experiments indicate a low surface concentration of phosphorus in the quaternized samples (Figure 6 and Table **I).** Since the elemental analysis indicates a high content of phosphorus in **all** the samples, one can infer

Figure 7. FT-IR spectrum of the porous nutshell particles containing adsorbed tetracarbonylcobalt species.

that the quaternary onium cations are hidden inside the polystyrene "cages".

There are several potential applications of this porous materials. They include the controlled release of **drugs** and the entrapment of highly active and toxic catalysts or reagents. Here we provide **as** an example the adsorption of cobalt carbonyl anions. This was accomplished by impregnating the dry quaternized substrate (containing poly[**(vinylbenzy1)tributylphosphonium** chloride) inside the particle; entry 2 in Table I) with an aqueous solution of tetracarbonylcobalt anions prepared by treating a $Co_2(CO)_8$ solution in benzene $(5.4 \times 10^{-2} \text{ M})$ with an aqueous solution of NaOH.⁹ After purification by extraction with CH_2Cl_2 for 24 h, the elemental analysis indicated a content of Co of 2.78 mmol/g of polymer, which exceeds the content of encapsulated phosphonium cations (0.83 mmol/g of) polymer). This implies that a large fraction of $NaCo(CO)₄$ complexes is physically adsorbed on the substrate. The FT-IR spectrum displays the characteristic absorption frequencies of the $Co(CO)₄$ --Bzl P⁺Bu₃ and NaCo(CO)₄ at 1746,1736,555, and 524 cm-' (Figure **7).** The deviations of the stretching frequencies of the carbonyl from the reported data¹⁰ 1888 and 555 cm⁻¹ (NaCo(CO)₄ in DMF) maybe attributed to the formation **of** ion pairs and to the different medium.

The polymer-supported bicatalyst prepared above has two structural characteristics: (1) a porous hydrophobic nutshell; **(2)** an encapsulated loose texture with pendant ion pairs $(Co(CO)₄ - -BzIP+Bu₃)$. Transition-metal carbonyl compounds constitute the most useful active species in catalyzing versatile organic reactions, especially under phase-transfer catalysis conditions.¹¹

Porous Hydrophilic Particles. The preparation of porous hydrophilic particles by suspension polymerization has been reported in patent form.¹² In the present paper a concentrated emulsion of water (containing a hydrophilic monomer and a cross-linking agent) in oil with Span-80 **as** emulsifier was employed to prepare hydrophilic particles. While three hydrophilic monomers have been tried (Table 11), only acrylamide and sodium acrylate formed stable concentrated emulsions.

The SEM picture (Figure 8a) shows that the hydrophilic porous spherical particles of polyacrylamide are of micron size and have a smooth surface. This morphology may be a result of a low extent of cross-linking, due to the small

⁽⁹⁾ Alper, H.; Aroumainian, H.; Petrignani, **J.-F.;** Manul, J. *J.* Chem. **SOC.,** *Chem. Commun.* **1985,340.**

⁽¹⁰⁾ Edgell, W. F.; Lyford, IV, J. *J. Chem. Phys.* **1970, 52, 4329.**

⁽¹¹⁾ (a) Alper, H. *Aldrichimica* **1991,24, 3.** (b) Brunet, J.-J. Chem. *Reu.* **1990, 1041.**

⁽¹²⁾ Mauz, 0.; Sauber, K.; Noetzel, S. **US.** Patent, **1985, 4,542,069.**

021006 25KV X**i0.0**K 3.0um B

(b) **(a)**

Figure 8. Scanning electron micrograph of polyacrylamide particles: (a) lightly cross-linked polyacrylamide particles; (b) particles with lightly cross-linked polyacrylamide nutshell encapsulating poly(E0).

Table II. Preparation of Hydrophilic Particles by			
Polymerizing Concentrated Emulsions of Water in Oil			

a AA, acrylamide; HEA, 2-hydroxyethyl acrylate; SA, sodium acrylate; PEG, poly(ethylene glycol), $M = 400$; MBAA, N,N-methylenebisacrylamide.

proportion of cross-linking agent and of the good solvating ability of water for polyacrylamide. The hydrophilic particles can be used **as** biocompatible substrates for the solid-phase synthesis of peptides¹³ as well as for immo-

(13) Bayer, E. Angew. Chem., Int. Ed. Engl. 1991,30,113.

bilization of enzymes. We observed, for instance, that these hydrophilic particles can adsorb 68 mg of lipase/g of polymer from an aqueous solution containing *0.5* mg of lipase / mL.

If the preparation procedure for hydrophilic particles is modified by first preparing a concentrated emulsion of w/o, in which the dispersed medium is **an** aqueous solution of poly(ethy1ene oxide), followed by the addition of acrylamide and MBAA and polymerization, a polyacrylamide shell that encapsulates the poly(ethy1ene oxide) *can* be generated (Figure 8b). This kind of material could be used in the controlled release of drugs, since if a biodegradable polymer (which is often water soluble) and drug molecules are encapsulated into the polyacylamide shell particles, the releasing process **can** be controlled through the degrading action of a specific enzyme present in the body.

Acknowledgment. This work was supported by the National Science Foundation.

Registry No. DVB/ST (copolymer), **9003-70-7; VBC** (homopolymer), **9080-67-5; VBPC, 143105-99-1; MBAA/AA** (copolymer), 25034-58-6; PEO, 25322-68-3; Co₂(CO)₈, 10210-68-1; lipase, **9001-62-1.**