Binding Catalytic Sites to the Surface of Porous Polymers and Some Catalytic Applications

E. Ruckenstein* and L. Hong

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

Received July 9, 1991. Revised Manuscript Received October 29, 1991

Polymer chains of quaternary onium salt have been bound to the internal surface of porous cross-linked polystyrene using two procedures based on the concentrated emulsion polymerization method. In the first procedure, surfactant molecules soluble in hydrophobic media and possessing an allyl or an acryloyl group in their hydrophilic moiety were synthesized and employed as emulsifiers in the preparation of gellike concentrated emulsions of water in styrene–divinylbenzene (ST–DVB). After polymerization, the surfactant molecules are present on the internal surface of the porous cross-linked polystyrene with the head groups residing on the surface. The obtained porous polymer was swollen in a methylene dichloride solution of (vinylbenzyl)trialkylammonium (or phosphonium) chloride containing AIBN as initiator. Then the system was polymerized, and as a result, the polymer chains of the quaternary onium chloride became grafted to the surface vinyl groups of the porous polymer. In the second procedure, the functional monomer vinylbenzyl chloride (VBC), was introduced into a partially polymerized gellike concentrated emulsion of water in ST–DVB, prepared by using a conventional surfactant (Span-80). During subsequent polymerization, polymers of VBC became grafted to the surface of porous poly(ST–DVB). Further, the benzyl chloride groups of poly(VBC) were transformed to styrenic groups through the Wittig reaction, thus obtaining a porous poly(ST–DVB) with surface-bound vinylbenzyl groups. Polymer chains of (vinylbenzyl)trialkylphosphonium chloride were then anchored to the porous polymer as in the first procedure. To each of the two kinds of surface-functionalized porous polymers, mono-sodium-sulfonated triphenylphosphine [$Ph_2P(C_6H_4$-*m*-$SO_3Na)$] was attached to a fraction of the polymer chains of quaternary onium salt as a coordination ligand for palladium acetate $Pd(OAc)_2$. In this manner, two kinds of catalytic active sites, namely, quaternary onium groups and $Pd(OAc)_2$ complexes, were located on the internal surface of the porous polymers. The polymer-supported bicatalysts have been employed in a vinylation reaction. The reaction activities and selectivities of the polymer-supported catalysts and of their homogeneous counterpart have been compared.

Introduction

The location of chemical functional species on insoluble polymer surfaces represents an important aspect in the field of polymer-supported reagents or catalysts,[1] solid-phase synthesis,[2] and immobilized enzymes.[3] The concentrated emulsion polymerization method can offer an effective pathway for the preparation of polymer latexes[4a] or porous polymers[4b] and for the functionalization of their surfaces. A concentrated emulsion can be prepared by dispersing a hydrophobic (hydrophilic) liquid into a hydrophilic (hydrophobic) liquid containing a suitable surfactant which stabilizes the system by its adsorption on the surface of the droplets. 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 emulsion has the appearance and behavior of a gel, and this provides some advantages in handling. When the dispersed phase is a hydrophobic monomer and the continuous phase is water, agglomerated polymer latexes are obtained after polymerization. On the other hand, when the dispersed phase is water and the continuous phase is a hydrophobic monomer, a porous polymer is obtained after polymerization.

Here two strategies are suggested for locating chemical anchors on the internal surface of porous cross-linked polystyrene polymers. In the first strategy, two oil-soluble functionalized surfactants, allyl(bis[2-(10-undecenoyloxycarbonyl)ethylene]methyl)ammonium bromide (AUMA) or diethylene glycol acryloyl oleyl ether (DGAO), are employed as emulsifiers in the preparation of gellike concentrated emulsions of water in styrene–divinylbenzene (ST–DVB). After polymerization, porous polymers with or acryloyl as surface groups are obtained. In the second strategy, the functional monomer vinylbenzyl chloride (VBC) is added under stirring to a partially polymerized gellike emulsion of water in ST–DVB. During its subsequent polymerization, VBC becomes grafted to the internal surface of poly(ST–DVB). The surface-bound poly(VBC) units are converted to vinylbenzyl groups via the Wittig reaction. In both strategies, three kinds of vinyl groups, namely, allyl, acryloyl, or styrenic group, are located on the internal surface of porous cross-linked poly(ST–DVB). They have been used as anchors to bind, via grafting, polymer chains of quaternary(vinylbenzyl)trialkylammonium (or phosphonium) chlorides. Consequently, in these functionalized porous polymers, the soluble chains of quaternary onium polymers become immobilized on the surface of insoluble cross-linked polystyrene. Since the pendant chains of chemically reactive groups (chains of a quaternary onium salt in the present case) are often flexible,[5] they can generate multiple sites cooperative reaction environments. The surface-immobilized polymer chains of quaternary onium salt are further used as substrates for the attachment, via the formation of ion pairs, of sulfonated phosphine palladium complexes.

The emphasis in this paper is on developing ways, via surface grafting, for the surface functionalization of

---

* To whom correspondence should be addressed.

(1) Guyet, A. *React. Polym.* **1989**, *10*, 113. Ford, W. T.; Chandran, R.; Turk, H.; *Pure Appl. Chem.* **1988**, *60*, 395. Sherrington, D. C. *Chem. Ind.* **1991**, *7*, 15. Alami, S. W.; Le Maguer, D.; Caze, C. *React. Polym.* **1987**, *6*, 213. Nishikubo, T.; Kato, T.; Sugimoto, Y. *Macromolecules* **1990**, *23*, 3406.

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

(3) Aglietto, M.; Chiellini, E.; D'Antone, S.; Ruggert, G.; Solaro, R. *Pure Appl. Chem.* **1988**, *60*, 415. Kennedy, J. F.; Melo, E. H. M.; Jumel, K. *Chem. Eng. Prog.* **1990**, *86*, 81.

(4) (a) Ruckenstein, E.; Kim, K.-J. *J. Appl. Polym. Sci.* **1988**, *36*, 907. (b) Ruckenstein, E.; Park, J.-S. *J. Polym. Sci., Polym. Lett. Ed.* **1988**, *26*, 529.

(5) Pillai, V. N. R.; Mutter, M. *Acc. Chem. Res.* **1981**, *14*, 122.

0897-4756/92/2804-0122$03.00/0

polymer supports, which could be used in a variety of reactions. For illustration purposes, polymer-supported bicatalysts possessing a phase-transfer catalyst and a palladium catalyst have been employed in a Heck-type vinylation reaction.

Experimental Section

Main Reagents. Styrene (Aldrich, 99%), divinylbenzene (Aldrich, tech, 55%), and vinylbenzyl chloride (Kodak, para and meta isomeric mixture) were distilled under vacuum. Span-80 (sorbitan-monooleate, Fluka), Brij-92 (main component: diethylene glycol oleyl ether, Fluka), acryloyl chloride (Aldrich, 98%), ethyl methacrylate (Aldrich, 99%), iodobenzene (Aldrich, 98%), and the solvents employed were used without further purification.

Synthesis of Surfactants and Reagents. Allyl(bis[2-(10-undecenoyloxycarbonyl)ethylene]methyl)ammonium bromide (AUMA) was prepared by the procedure reported by Tundo and Fendler.[6]

Diethylene glycol acryloyl oleyl ether (DGAO): To stirred Brij-92 (33.65 g), 8.7 g of acryloyl chloride (94 mmol) was added over 30 min, at room temperature. The mixture was then kept stirring, in a water bath, for 5–6 h at 50–60 °C. The generated HCl was allowed to pass out through a drying tube containing calcium chloride. The solution was evaporated under heating to remove the unreacted acryloyl chloride and the dissolved HCl using a water vacuum pump. A viscous yellow liquid was thus obtained.

Vinyl-$PhCH_2N^+R_3Cl^-$ (R = Et, Bu) (VEAC, VBAC), Vinyl-$PhCH_2P^+Bu_3Cl^-$ (VBPC): These three quaternary onium salts were synthesized according to reported methods.[7]

m-Sodium sulfonated phenyldiphenylphosphine, *m*-$NaO_3S-C_6H_4PPh_2{-}2H_2O$ (mSPDP): The synthesis was performed by using a well-known method.[8]

Preparation of Porous Polymers. Porous cross-linked polystyrene possessing surface allyl (I) or acryloyl (II) groups: A gellike concentrated emulsion was prepared by dropwise addition of 30 mL of water to a styrene (3.65 g)/divinylbenzene (0.8 g) mixture, containing 10 mg of AIBN and either 1.0 g of AUMA or 0.4 g of Span-80 and 2.0 g of DGAO, under mechanical stirring (using a Teflon blade at about 500 rpm), over about 20 min, at room temperature. The gel was introduced in glass tubes of 25-mL capacity, which were shaken with a mixer to achieve a tighter packing of the gel. Then the tubes were sealed with rubber taps and filled with nitrogen, and the systems were polymerized by heating for 64 h at 40–45 °C. The porous polymers were ground and washed three times by their stirring in methanol–acetone mixtures (1 h each time) at 40–50 °C. After vacuum drying, porous polymer materials containing allyl groups (when AUMA was used as surfactant) or acryloyl groups (when Span-80/DGAO were employed as surfactants) were obtained.

Porous cross-linked polystyrene with surface-grafted vinyl benzyl polymer chains (III): To a stirred styrene (3.65 g)/divinylbenzene (0.8 g) mixture containing 15 mg of AIBN and 1.0 g of Span-80, 30 mL of water was added dropwise under the conditions mentioned above. The flask containing the prepared gellike concentrated emulsion was sealed, filled with nitrogen, and immersed into a water bath at 40 °C for polymerization. After 16 h of polymerization, the partially polymerized gellike concentrated emulsion was cooled to room temperature. Then 1.04 g of vinylbenzyl chloride was added dropwise with a 5-mL syringe under vigorous stirring (about 700 rpm) over about 10 min. The gel was subsequently packed into glass tubes and further polymerized in a 40 °C water bath, under the protection of nitrogen, for 48 h. A porous cross-linked polystyrene with surface-grafted poly(vinylbenzyl chloride) was thus prepared. The obtained material was purified by grinding it into a powder and stirring the powder three times in a methanol–acetone mixture, at 40–50 °C, and then once in refluxing ethanol (1 h each time). After drying, 2.85 g (1.20 mmol of Cl/g) of porous polymer powder together with 5.70 g (21.7 mmol) of triphenylphosphine was added to 40 mL of DMF. The suspension was stirred under a nitrogen atmosphere in an oil bath for 4 days at 100 °C. After this was cooled, 60 mL of petroleum ether was added and the system was stirred for a few minutes. The filtrated polymer was extracted with THF for 2 h in a Soxlet condenser and then dried under vacuum at room temperature, overnight. The polymer-supported Wittig reagent (3.65 g) suspended in 40 mL of formaldehyde (38%) in a 150-mL flask, and 6 mL of NaOH aqueous solution (50 wt %) was added dropwise to the stirred suspension. After the addition of NaOH, the system was stirred at room temperature for 15 h under a nitrogen atmosphere. The surface-vinylized porous polymer was filtrated in a Buchner funnel and washed with water three or four times. The purification was carried out by stirring the polymer in methanol three times and in acetone two times (0.5 h each time) at 40–50 °C. Finally, the obtained material was vacuum dried.

Quaternization of the Porous Polymer through the Grafting Reaction of (Vinylbenzyl)trialkylammonium or -phosphonium Chloride to the Surface Vinyl Groups. The surface-functionalized porous polymer I, II, or III (1 g) was added to 10 mL of dichloromethane solution (0.3 M) of a quaternary onium chloride (VEAC, VBAC, or VBPC) containing 10 mg of AIBN, in a 25-mL tube. The swollen polymer was first subjected to ultrasonic treatment under a nitrogen flow for a few minutes to remove the oxygen and subsequently allowed to polymerize under a nitrogen atmosphere for 48 h in a water bath at 40 °C. The resulting polymers were thoroughly washed several times with methanol and subsequently with chloroform.

Attachment of mSPDP and Palladium Diacetate to the Porous Polymer Containing Surface-Grafted Polymer Chains of Quaternary Onium Chloride. Typical procedure: The surface-quaternized polymer III (1 g; 0.97 mmol of P/g) was suspended under stirring, at room temperature, in a mixture of ethanol (6 mL) and water (8 mL) containing 0.2 g of mSPDP (0.54 mmol), overnight. The treated polymer was washed with water several times in a Buchner funnel and then dried. The polymer was further immersed into a solution (1.24×10^{-2} M) of palladium diacetate in 10 mL of THF. After stirring for 30 min, the polymer was filtered and washed several times by stirring in THF and subsequently overnight in 20 mL of benzene, at room temperature. The filtrated benzene remained colorless. A polymer-supported bicatalyst was thus obtained.

Vinylation Reaction of Iodobenzene with Ethyl Methacrylate. Typical procedure: A mixture of ethyl methacrylate (0.94 g, 8.2 mmol), iodobenzene (1.38 g, 6.6 mmol), potassium carbonate (1.0 g, 7.2 mmol), and polymer III supported bicatalyst (0.3 g, 0.29 mmol of phosphonium, 7.2×10^{-2} mmol of sulfonated phosphine, and 2.4×10^{-2} mmol of Pd) in 10 mL of DMF (anhydride) was heated under stirring in an oil bath (55–60 °C), for 20 h, under a nitrogen atmosphere. The vinylation products were analyzed by HPLC (ISCO-2350 pump/ISCO-V_4 (UV-248 nm) detector: 4.6 mm × 25 cm column filled with Adsorbosphere C_8 of 5 μm.

Results and Discussion

Surfactant Anchors for Binding Functional Groups to the Surface of Porous Polymers.

The functionalization of the surface of insoluble polymer supports is a currently employed procedure. Recently, Menger and Tsuno[9] reported a method for preparing porous polymeric supports starting from microemulsions containing 10–20 vol % water in a styrene–divinylbenzene (ST–DVB) mixture. The surfactant employed for the stabilization of the microemulsion contained a polar group of diamine which could be used as a ligand for coordinating Cu^{2+} ions. In the present paper, the concentrated emulsion polymerization method[4] is employed to carry out the

---

[6] Tundo, P.; Kippenberger, D. J.; Klahn, P. L.; Prieto, N. E.; Jao, T.-C.; Fendler, J. H. *J. Am. Chem. Soc.* **1982**, *104*, 456.

[7] Nishikubo, T.; Uchida, J.; Matsui, K.; Iizawa, T. *Macromolecules* **1988**, *21*, 1583. Brandstrom, A.; Ldamon, B. *Acta Chem. Scand.* **1974**, *B28*, 590.

[8] Ahrland, S.; Chatt, J.; Davies, N. R.; Williams, A. A. *J. Chem. Soc.* **1958**, 276.

[9] Menger, F. M.; Tsuno, T.; *J. Am. Chem. Soc.* **1990**, *112*, 1263; **1990**, *112*, 6723.

Table I. Preparation via the Concentrated Emulsion Polymerization Method of Porous Cross-Linked Polystyrene Substrates Possessing Surface Allyl or Acryloyl Groups

			surfactant, g			IR characterization of surfactants attached to the surface of the pores, cm^{-1}
porous polym	ST-DVB, g	H_2O, mL	Span-80	AUMA	DGAO	
I	3.65–0.80	30		1.00		1732
II	3.65–0.80	30	0.45		2.00	1735, 1710

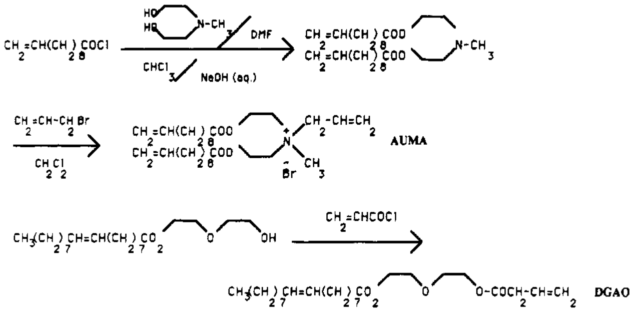


Figure 1. Synthesis of the surfactants AUMA and DGAO.

Table II. Elemental Analysis of Porous Polymers Containing Surface-Anchored Polymer Chains of Quaternary Onium Chloride as Well as of Those Containing mSPDP and Pd Complexes[a]

compn	IaP-Pa	IIaP-Pd	IIpP-Pd	IIIpP-Pd
polym substrate	I	II	II	III
bound onium group	VBAC	VEAC	VBPC	VBPC
phosphine ligand	mSPDP	mSPDP	mSPDP	mSPDP
contents of heteroatoms, mmol/g of polymer				
N (IV)	0.31	1.08		
P (IV)			0.60	0.97
P (III)	0.07	0.44	0.10	0.24
Pd (II)	0.04	0.09	0.05	0.08

[a] N (IV) denotes the quaternary ammonium groups, P (IV) the quaternary phosphonium group; P (III) denotes the mSPDP.

surface functionalization of the polymer by using "tailed" surfactants. These surfactants stabilize the gellike concentrated emulsions of water in hydrophobic monomers and allow the attachment of chemical anchors to the internal surface of the porous polymers.

The present method involves two steps: In the first, porous cross-linked polystyrene substrates with surface allyl or acryloyl groups are prepared via the concentrated emulsion polymerization method. The concentrated emulsion contains a large volume fraction (0.86 in this case) of water as dispersed phase and a low volume fraction of styrene–divinylbenzene–AIBN as the continuous phase. The large volume fraction of water generates after polymerization a material with large pores easily accessible to reactants. The continuous phase also contains a surfactant with an allyl group {allyl(bis[2-(10-undecenoyloxycarbonyl)ethylene]methyl)ammonium bromide, AUMA} or a mixture of sorbitan monooleate (Span-80) and a surface-active compound with an acryloyl group (diethylene glycol acryloyl oleyl ether, DGAO; Figure 1 and Table I). The DGAO does not lead alone to a stable concentrated emulsion; for this reason its combination with Span-80 was necessary. The allyl or acryloyl group bearing hydrophilic moieties of the surfactants are oriented into the water phase at the oil/water interface. Two porous polymer materials [denoted as I (containing allyl groups) and II (containing acryloyl groups)] were obtained after polymerization (Table I and Figure 2). The presence of surfactant molecules in the porous polymers was identified by IR. We observed that only a suitable amount of AUMA allowed polymerization to occur. If the amount was too low, gellike emulsions could not be generated; if the amount was too large, the polymerization of the formed gellike emulsions was inhibited. This is perhaps because AUMA is a double-chain surfactant that can form vesicles in water.[10] When the amount used is large, a fraction of AUMA may aggregated as vesicles and the polymerization may be inhibited because the initiator AIBN is trapped into the vesicles.

In the second step, the obtained porous polymers were immersed into a CH_2Cl_2 solution of a quaternary onium

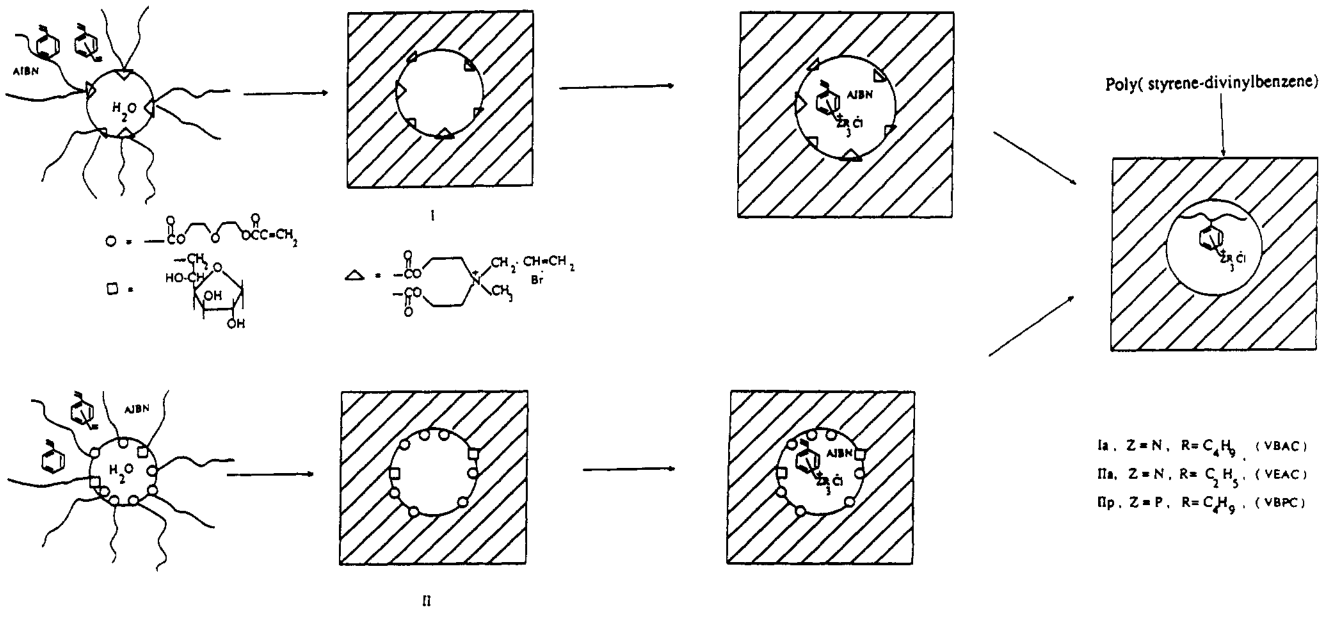


Figure 2. Preparation of porous polymer-supported poly(quaternary onium salts) using surfactants as anchors.

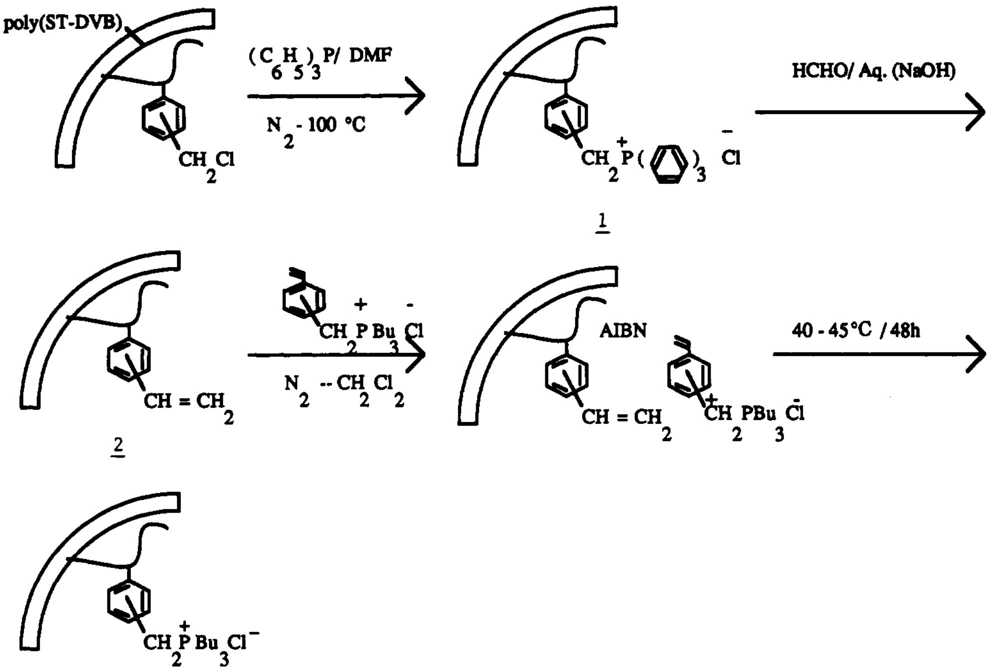


Figure 3. Preparation of porous polymer-supported poly(VBPC) using surface-grafted poly(VBC) as anchors.

monomer (VEAC, VBAC, or VBPC) containing AIBN. When the swollen polymers were subjected to polymerization, the quaternary onium monomers were polymerized and simultaneously grafted to the surface allyl or acryloyl groups. Three kinds of functionalized polymers containing poly(VBAC) (denoted Ia), poly(VEAC) (denoted IIa), and poly(VBPC) (denoted IIp) depicted in Figure 2 were prepared.

The elemental analysis of the purified polymers (Table II) showed that a fraction (about 5 mol % for I, 36 mol % for II) of quaternary ammonium monomer introduced in the system was chemically bound to the internal surface of the porous polymer. Hence the combination between the nonionic surfactant Span-80 and DGAO facilitates the surface functionalization more than AUMA. For this reason we synthesized another surfactant {(vinylbenzyl)(bis[2-(10-undecenoyloxycarbonyl)ethylene]-methyl)ammonium bromide, VUMA}, in which the allyl group of AUMA was replaced by the vinylbenzyl group. However, this surfactant could not generate stable concentrated emulsions at room temperature.

The selection of the reaction solvent for performing the surface functionalization is an important factor. We have observed that when the solvent CH_2Cl_2 was replaced with DMF/H_2O (v/v = 3:1), the quaternary onium monomers could not be anchored to the porous polymers. It is possible that the wetting ability of the solvent for the surface of the porous poly(styrene–divinylbenzene) plays a role in the anchoring of various species to the polar head groups of the surfactant molecules.

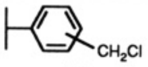
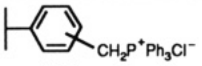
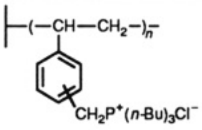
Grafting Poly(VBC) Chains on the Internal Surface of Porous Poly(ST–DVB) for Further Functionalization by Using Partially Polymerized Concentrated Emulsions. The selection of a surfactant as an anchor for binding quaternary onium monomers to the surface of porous polymers should satisfy two requirements: (a) the stability of the concentrated emulsion and (b) the presence of desired groups on its polar head for further chemical transformation. There are difficulties in satisfying simultaneously both requirements, since when a functionalized surfactant is employed, a concentrated emulsion may not form. For this reason we propose the functionalization of the surface be carried out directly via grafting of poly(VBC) to the surface of poly(ST–DVB). A conventional surfactant (such as Span-80) was used to prepare the concentrated emulsion (Table III). Two steps were employed: First, a concentrated emulsion of water in ST–DVB (volume fraction of water = 0.86) was partially polymerized (16 h at 40 °C); a highly viscous gel was thus obtained. Second, a certain amount of vinylbenzyl chloride (VBC) was added slowly to this partially polymerized gel, under vigorous stirring, to ensure the uniform distribution of VBC into the gel. Finally, the obtained gel was completely polymerized. The higher the viscosity of the partially polymerized concentrated emulsion, the more attenuated is the diffusion of VBC molecules inside the partially polymerized system. Therefore most of the VBC molecules will polymerize among themselves as well as with ST/DVB molecules present on the internal surface. The further functionalization of the porous poly(ST–DVB) with grafted poly(VBC) chains on the internal surface includes the formation of pendant triphenyl benzyl phosphonium chloride 1 and pendant vinyl benzyl group 2 via the Wittig reaction (Figure 3 and Table III). The surface-pendant vinyl benzyl groups of the porous polymer were used as effective anchors to bind quaternary onium groups through the grafting reaction discussed in the previous section. A comparison of SEM pictures of the porous polymers containing pendant vinylbenzyl groups (Figure 4a) and porous polymers containing grafted polymer chains of vinylbenzyl tributyl phosphonium chloride (VBPC; Figure 4b; this polymer is denoted as IIIp) reveals the presence of numerous small nubbles grown on the internal surface of the latter porous polymer. It is likely that they represent the grafted polymer of VBPC.

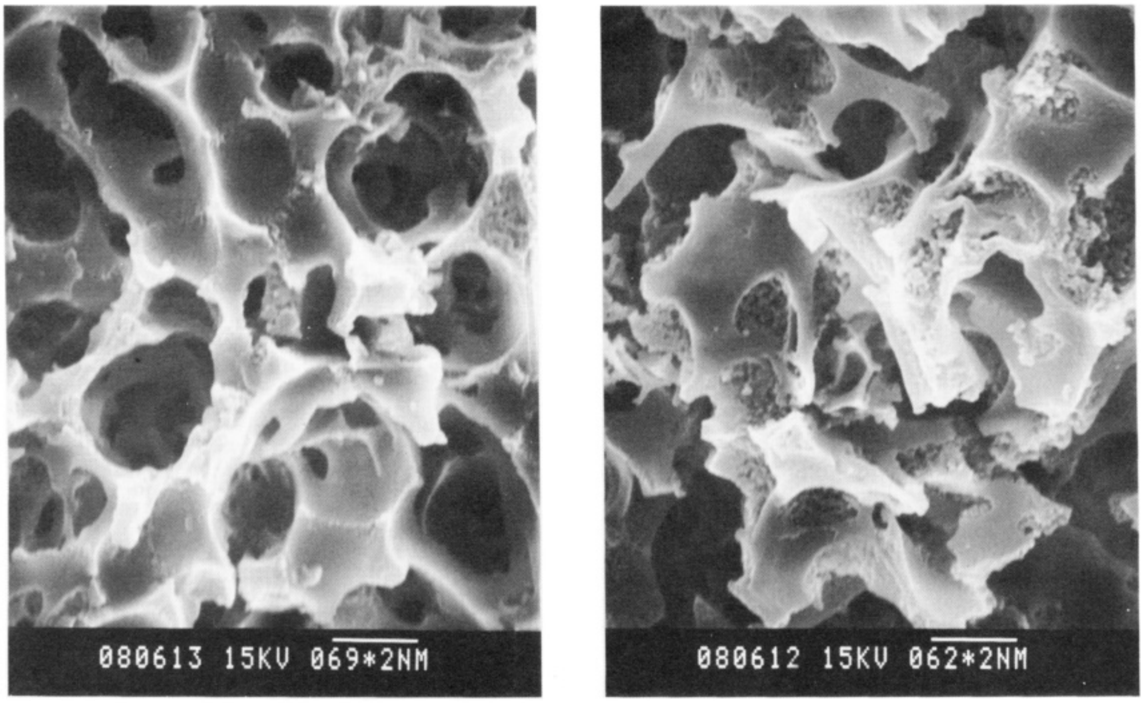
Two advantages in the application of this method should be noted: (1) one can select and even combine functional monomers other than VBC as "precursory anchors" as long as they are hydrophobic, such as organophosphine monomers; (2) the number of pendant functional groups in the polymer chains grafted on the surface is larger than for

---

(10) Fendler, J. H. *Chem. Rev.* **1987**, 877.

Table III. Preparation via Concentrated Emulsion Polymerization Method of Porous Cross-Linked Polystyrene with Surface-Grafted Poly(VBC) and the Elemental Analysis of Its Subsequently Functionalized Forms

compn of the conc emulsion			polym		
			 III	 Wittig reagent	 III p
ST-DVB, g	H_2O, mL	VBC, g	mmol of Cl/g	mmol of P/g	mmol of P/g
3.65–0.80 (35–3.3 mmol)	30	1.04 (6.28 mmol)	1.20	0.92	0.97



(a) (b)

Figure 4. Scanning electron micrograph of (a) polymer III and (b) polymer IIIp.

surfactant anchors. For example, polymer III contains 1.20 mmol of pendant benzyl chloride group/g of polymer, while in polymer II the maximum content of acryloyl groups is 0.5 mmol/g of polymer. In addition, the amount of functional monomers can be more easily varied for matching the requirements than the amount of surfactant, since a too large amount of surfactant can hinder the formation of a concentrated emulsion.[11]

Heterogeneous Vinylation Reaction of Iodobenzene with Ethyl Methacrylate. The palladium catalyst employed in the Heck-type reaction[12] was combined[13] with a phase-transfer catalyst (PTC) to provide an efficient method for the preparation of styrene derivatives in a homogeneous system, under mild conditions. The heterogenization of this homogeneous bicatalytic process is examined in what follows. Although polymer-supported transition-metal catalysts[14] and polymer-supported PTC[15] systems have been widely used, there are few examples in which both a transition-metal catalyst and a PTC were supported on the same polymer.[16] We prepare a polymer-supported bicatalytic system by attaching a negatively charged phosphine compound, m-sodium-sulfonated phenyldiphenylphosphine (mSPDP), to a fraction of the pendant polymer chains of quaternary onium groups. The attached phosphine compound was subsequently coordinated with palladium. Four polymer-supported catalysts (denoted IaP–Pd, IIaP–Pd, IIpP–Pd, and IIIpP–Pd, where P denotes the mSPDP), listed in Table II were employed to catalyze the vinylation reaction

$$C_6H_5I + CH_2{=}C(CH_3)CO_2Et \rightarrow \underset{Z \text{ and } E}{C_6H_5CH{=}C(CH_3)CO_2Et} + \underset{\text{regio isomer}}{C_6H_5CH_2C(CH_2)CO_2Et}$$

---

(11) Chen, H. H.; Ruckenstein, E. *J. Colloid. Interface Sci.* **1991**, *145*, 260.

(12) Patel, B. A.; Ziegler, C. B.; Cortese, N. A.; Plevyak, J. E.; Zebovitz, T. C.; Terpko, M.; Heck, R. F. *J. Org. Chem.* **1977**, *42*, 3903. Heck, R. F. Palladium Reagents in Organic Synthesis; Academic Press: New York, 1985.

(13) Jeffery, T. *J. Chem. Soc., Chem. Commun.* **1984**, 1287. Miura, M.; Hashimoto, H.; Itoh, K.; Nomura, M. *J. Chem. Soc., Perkin. Trans.* **1990**, *1*, 2207. Gore, E. S. *Plat. Met. Rev.* **1990**, *34* (1), 2. Pugh, C.; Percec, V. *Chem. Mater.* **1991**, *3*, 107.

(14) Pittman, C. U. *Comprehensive Organometallic Chemistry*; Wilkinson, G., Ed.; Pergmon Press: Oxford, 1982. Sherrington, D. C., Hodge, P., Eds. *Syntheses* and *Separations Using Functionalized Polymers*; Wiley: New York, 1988.

(15) Freedman, H. H. *Pure Appl. Chem.* **1986**, *58*, 857. Svec, F. *Ibid.* **1988**, *60*, 377.

(16) Blanton, J. R.; Salley, J. M. *J. Org. Chem.* **1991**, *56*, 490.

Table IV. Use of Four Porous Polymer-Supported Catalysis in the Vinylation Reaction of Iodobenzene with Ethyl Methacrylate (EMA)[a]

run	catal (amount used, g)	yield of the vinylation reaction,[c] mol %	
		(Z,E)-PhCH=C(Me)CO$_2$Et	PhCH$_2$C(=CH$_2$)CO$_2$Et
1	IaP-Pd (0.45)	27	2
2	IIaP-Pd (0.30)	34	2
3	IIpP-Pd (0.35)	26	3
4	IIIpP-Pd (0.30)	36	negligible
5	Pd(mSPDP)[b] BzlP$^+$Bu$_3$Cl$^-$	26	4

[a] The reaction was carried out in 10 mL of DMF containing polymer-supported bicatalysts (the composition of the catalysts are given in Table II), 1.0 g of K$_2$CO$_3$, PhI (6.5 mmol), and EMA (8.2 mmol) by heating for 20 h under N$_2$ atmosphere at 55–60 °C. [b] Pd(OAC)$_2$ (6.7 × 10^{-2} mmol), mSPDP (1.3 × 10^{-1} mmol), Bzl-P$^+$Bu$_3$Cl$^-$ (0.24 mmol). [c] The analysis was carried out using HPLC.

Preliminary heterogeneous catalytic results are listed in Table IV (runs 1–4), which also contains the homogeneous catalytic result (run 5). The concentration and the structure of the pendant quaternary onium groups affect the yield and the regioselectivity of the reaction. In runs 2 and 4 (where IIaP–Pd and IIIpP–Pd were used) the yield is higher than in runs 1 and 3 (where IaP–Pd and IIpP–Pd were used), because the concentrations of the pendant quaternary onium salts are higher in the former than in the latter catalysts. The pendant quaternary ammonium salt generates a somewhat greater amount of the regioisomer than the pendant quaternary phosphonium salt.

To investigate in more detail the reactivity of the porous polymer supported bicatalysts, catalyst IIIpP–Pd was chosen to examine the kinetics of the reaction. For comparison purposes, the homogeneous counterpart under the same conditions was also investigated. The results are presented in Figure 5 and show that during the initial 10 h of reaction there is no difference in the rates for the two systems. This indicates that in the heterogeneous case the diffusion process inside the catalyst does not play a role. This can be explained by the high porosity and hence the high accessibility of the catalytic sites to the reactants.

The tendency to form an ion pair between the negatively charged phosphine ligand and positively charged quaternary onium group has been utilized to bind the former to the polymer substrate. The stability of this ion pair is, therefore, crucial in the practical application of the polymer catalyst. If mSPDP is replaced by P(C$_6$H$_4$-m-SO$_3$Na)$_3$, the ionic attraction to the quaternary onium sites will be greater. A negative feature of mSPDP is that its sulfonated group can also coordinate with palladium by replacing the original acetate groups. This breaks the link between the quaternary onium group and mSPDP, thus detaching Pd from the substrate.

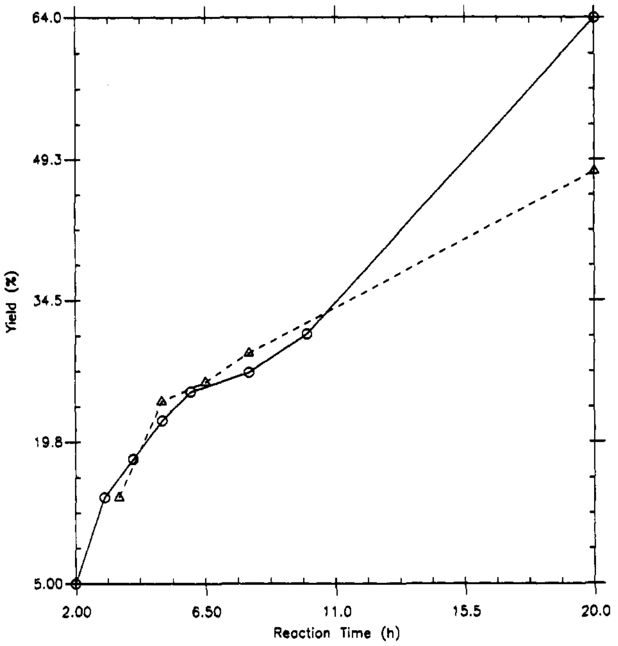


Figure 5. Comparison of the catalytic activities of polymer-supported catalyst III pP-Pd (○); homogeneous counterpart BzlP$^+$Bu$_3$Cl$^-$ and Pd(OAc)$_2$ (△). The reaction conditions are as follows: (1) for the heterogeneous system 0.8 g of IIIpP-Pd was used; (2) for the homogeneous system 0.26 g of BzlP$^+$Bu$_3$Cl$^-$ (0.79 mmol) and 0.016 g (7.1 × 10^{-2} mmol) of Pd(OAc)$_2$ (compatible amounts with those in heterogeneous system) were used. The other conditions are the same in both cases: 1.0 g of K$_2$CO$_3$, PhI (7.0 mmol), and EMA (8.5 mmol) in 10 mL of DMF, reaction temperature 55 °C under N$_2$ atmosphere.

Summary

Three kinds of surface-functionalized porous poly(ST–DVB) have been prepared by employing the concentrated emulsion polymerization method. The strategies employed for the surface functionalizations have been based on (1) the use of surfactants that possess allyl or acryloyl groups in their polar head groups in the preparation of water in oil (w/o) concentrated emulsions and (2) the introduction of the functional monomer VBC into partially polymerized concentrated emulsions (w/o) and allowing the resulting emulsions to completely polymerize. The further chemical modifications of the surface benzyl chloride groups prepared by the second strategy involve their convertion to pendant vinyl benzyl groups. The three kinds of porous polymers thus prepared prossess an allyl, acryloyl, or vinylbenzyl group on their internal surface. Polymeric chains of quaternary ammonium or phosphonium salts are grafted to the surface of these three porous polymers through the polymerization of the monomers (VEAC, VBAC, VBPC) and their simultaneous grafting with the surface-pendant double bonds. Pd(OAc)$_2$–(mSPDP) complexes have been attached to a fraction of the polymer chains of quaternary onium salts. The polymer-supported bicatalysts containing palladium phophine complexes (coordinative catalyst) and quaternary onium groups (PTC) have been employed in a vinylation reaction. A comparison with the homogeneous reaction revealed the absence of diffusion limitation in the heterogeneous system.

Registry No. EMA, 97-63-2; DGAO, 137870-27-0; Brij-92, 9004-98-2; PhI, 591-50-4; PhCH=C(Me)CO$_2$Et, 1734-78-7; PhCH$_2$C(=CH$_2$)CO2Et, 20593-63-9; H$_2$C=CHCOCl, 814-68-6.