

Metal carbonyl anion loaded molecular reservoir particles – application to the catalytic synthesis of two styrene oxide derivatives

Liang Hong, Eli Ruckenstein *

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

Received 15 November 1994; accepted 24 March 1995

Abstract

Molecular reservoirs consisting of a porous polydivinylbenzene (PDVB) nutshell surrounding polytriethylvinylbenzyl ammonium chloride (PEVAC) chains were employed to immobilize the homogeneous catalysts: $[\text{Co}(\text{CO})_4]^-$ or $[\text{Rh}(\text{CO})_2\text{I}_2]^-$. The molecular reservoirs were prepared by the successive polymerization of vinylbenzyl chloride (VBC) and divinylbenzene (DVB) in a concentrated emulsion, followed by the quaternization of the encapsulated VBC chains. The immobilization was achieved via the formation of ion-pairs between the ammonium cations and the metal carbonyl anions. Two kinds of polymer-bound catalysts dispersed in water were used to catalyze the synthesis of two derivatives of styrene oxide in the presence of CO. It was found that when PDVB (PEVAC)- $[\text{Co}(\text{CO})_4]^-$ was used, 2,5-dihydro-2-oxo-3-hydroxy-4-phenylfuran was the main product, as in the homogeneous case. When, however, PDVB(PEVAC)- $[\text{Rh}(\text{CO})_2\text{I}_2]^-$ was employed, 2-phenyl-2-(α -styryloxy)ethanol was obtained as the main product; in the homogeneous case, the selectivity was much lower. Both polymer-bound catalysts were used in five successive cycles at 200 psi CO and 95–98°C, and the conversion of styrene oxide was almost quantitative. The cocatalyst methyl iodide was introduced before the first cycle only. It was found that 72% of the initial Co and 94% of the initial Rh were still present in the molecular reservoirs after the five cycles. In addition to immobilizing the homogeneous catalyst, the molecular reservoir PDVB(PEVAC) also possesses some adsorption capability for the organic reactant molecules, because of its hydrophobic porous PDVB shell. This hydrophobic adsorption capability allows the styrene oxide molecules to approach the encapsulated catalytically active sites.

1. Introduction

Homogeneous catalyzed reactions between carbon monoxide and organic compounds have provided more effective routes to some commercially important compounds than conventional organic synthesis methods [1]. The low-valent carbonyls of Group VIII metals were found to be catalysts for the carbonylation of alkenes and alkynes [2]; carboxylation of acetylene [3], methanol [4],

organic halides [5], and olefins [6]; olefin isomerization [7]; isocyanation of aromatic nitrocompounds [8] and coupling reactions [9]. The cobalt and rhodium compounds are especially important homogeneous catalysts. For instance, $[\text{Co}(\text{CO})_4]^-$ and $[\text{Rh}(\text{CO})_2\text{I}_2]^-$, which are prepared by treating $\text{Co}_2(\text{CO})_8$ and RhCl_3 with iodine compounds under a CO atmosphere, are presumed to be the active homogeneous catalysts for the carbonylation and carboxylation reactions [10]. However, a number of major problems make the use of these metal carbonyls difficult:

* Corresponding author.

(1) they are dangerous to the environment; (2) they are very expensive; (3) the active catalytic species tend to agglomerate during reaction. Immobilization of the catalytically active species on suitable supports constitutes an effective solution for the above difficulties [11], since the supported metal carbonyls are reusable and the active sites are fixed on the support.

The typical catalyst supports are in the form of porous inorganic [12] or polymer [13] particles with high internal surface area. In this paper, a polymer molecular reservoir (micro-size particles) consisting of a porous poly(divinylbenzene) (PDVB) nutshell encapsulating poly(triethylvinylbenzyl ammonium chloride) chains (PEVAC) was employed as support. This special architecture was achieved by the concentrated emulsion polymerization method [14]. This kind of support is particularly suitable for organic/water two-phase catalytic systems, since the hydrophobic porous shell facilitates the diffusion of the organic reactants and products, and also prevents leakage of the hydrophilic PEVAC chains. When fully swollen by water, the encapsulated hydrophilic linear quaternary onium chains provide flexible multiple binding sites for the metal carbonyl anions.

In order to demonstrate the usefulness of the polymer molecular reservoirs, henceforth denoted as PDVB(PEVAC), in the immobilization of metal carbonyl anions, we examined the reactions of styrene oxide in the presence of CO catalyzed by supported $[\text{Co}(\text{CO})_4]^-$ or $[\text{Rh}(\text{CO})_2\text{I}_2]^-$ in an organic/water two phase system.

2. Experimental

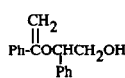
2.1. Reagents

Most of the chemicals were purchased from Aldrich. 3 and 4-Vinylbenzyl chloride (VBC) (98%) and divinyl benzene (DVB) (Fluka, 70–80%) were passed through an inhibitor removal column before use. The initiator, azobisisobutyronitrile (AIBN) (Kodak, tech.), was recrystal-

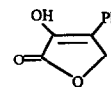
lized from methanol before use. Triethylamine (99%), sodium dodecylsulfate (SDS) (99%), styrene oxide (99%), *sec*-phenethyl alcohol (99%), methyl iodide (99%), rhodium chloride hydrate, cobalt carbonyl (Fluka, 98%), hexadecyltrimethylammonium bromide (CTAB) (Fluka, >99%), sodium hydroxide (97%), carbon monoxide (CS Gases Inc.) and organic solvents were used without further purification. Silica gel (TLC high-purity grade, without binder) was used in the chromatographic separation.

2.2. Instruments

A 150-ml high pressure reactor (Parr 4841) was employed for the reaction. Energy dispersive spectroscopy surface analysis (EDS) was performed with a PGT/IMIX field emission electron microscopy equipment. The morphology of the molecular reservoir was investigated with a scanning electron microscope (SEM) (Hitachi S-800). The infrared spectra of the immobilized polymer catalyst powders and of the products were obtained with an Alpha Centauri FT-IR instrument using a KBr cell. $^1\text{H-NMR}$ spectra of the products were recorded on a VXR-400 spectrometer, using chloroform-*d* as solvent. The molecular weights of the products were determined with a VG Analytical SE-70 spectrometer, using the chemical ionization method with isobutane as the source of the reactant ion. The conversion and the products were determined using a HPLC [Isco-2350 pump/Isco- V_4 (UV 254 nm)] containing an Adsorbosphere C_8 , 5μ (Alltech) filled column (I.D. 4.6 mm, length 150 mm). The mobile phase employed was a mixture of 70% acetonitrile and 30% water (v/v). The elemental analysis was carried out by Quantitative Technologies Inc. Whitehouse, NJ.



2-phenyl-2-(α -styryloxy)ethanol



2,5-dihydro-2-oxo-3-hydroxy-4-phenylfuran

Scheme 1. Compounds prepared.

2.3. Preparation of the porous nutshell molecular reservoirs

Preparation of the poly(divinylbenzene)-poly(vinylbenzyl chloride) (PDVB-PVBC) porous nutshell particles

SDS (0.5 g) dissolved in 4 ml water was first introduced in a 100 ml round bottom flask. A solution containing 2 g of vinylbenzyl chloride and 50 mg of AIBN dissolved in a mixture of a nonpolar (octane) and more polar (toluene) solvent (10 ml/10 ml), was added dropwise with mechanical stirring (≈ 700 rpm) to the aqueous solution. A concentrated emulsion of oil in water was thus obtained as a white paste. Then the flask was filled with nitrogen and immersed in a water-bath (40°C) for 16 h to effect the polymerization of the VBC. Subsequently, divinylbenzene (2 g) was slowly introduced, also with vigorous stirring, into the emulsion containing toluene-swollen PVBC surrounded by octane. Octane does not swell the PVBC but dissolves DVB. After additional mixing, the concentrated emulsion was packed into glass tubes sealed with septa. The polymerization of the DVB was carried out under N₂ in a water bath at 40–45°C for 16 h and at 60–65°C for another 8 h. The emulsion was thus converted to PDVB-PVBC latexes, which were precipitated by addition to methanol, washed several times with hot water and methanol, and finally dried in air at the ambient temperature to obtain 3.8 g of PDVB-PVBC powder. The elemental analysis indicated that the content of chlorine was 3.1 mmol/g of the powder.

Preparation of poly(DVB)-poly(triethyl benzyl ammonium chloride) PDVB(PEVAC)

A suspension of 3.0 g of PDVB-PVBC powder in 15 ml DMF was prepared in a 100 ml flask, and 3 ml triethylamine was added. The mixture was stirred for about 2 days in an oil bath (55–65°C) to generate pendant triethylbenzylammonium chloride groups. After reaction, 20 ml of THF and petroleum ether (60 ml) were successively introduced to extract the DMF and to precipitate the functionalized latexes, PDVB(PEVAC). The

upper part of the liquid was decanted and a mixture of THF-petroleum ether was added to wash the powder. The purification was repeated 3–4 times. After filtering and drying, 3.8 g of PDVB (PEVAC) powder was obtained.

2.4. Dimerization of styrene oxide using PDVB (PEVAC)-[Rh(CO)₂I₂]⁻ as catalyst

PDVB(PEVAC) powder (1.5 g) was dispersed in a solution of RhCl₃ · 3H₂O (60 mg, 0.23 mmol) in 45 ml of water, in a Parr high-pressure reactor. Styrene oxide (7.2 g, 60 mmol) and 1 ml of methyl iodide were introduced into the aqueous solution. After the system was purged three times at room temperature with CO (5–10 psi) with slow stirring, CO was introduced until a pressure of 200 psi was achieved. The reaction was conducted with stirring at 95–98°C for 18 h. After reaction, about 40 ml of cyclohexane was added to the system, followed by stirring for a few minutes to extract the organic compounds. The system was then filtered to separate the immobilized polymer catalyst. The latter changed from yellowish in color to coffee-like when exposed to air. The organic phase was separated from the aqueous phase in a funnel, and concentrated by evaporating the cyclohexane. The remaining oil contained only a very small amount of styrene oxide (by HPLC). The major product, a colorless oil (2.8 g) was separated by elution through a silica gel column using a mixture of ether and petroleum ether. FT-IR, ¹H-NMR and MS analysis indicated that the compound was 2-phenyl-2-(α -styryloxy)ethanol (Scheme 1). FT-IR: 2600–3100 cm⁻¹, w (ν_s OH); 3030, 3036 and 3086 cm⁻¹ m (ν_s unsaturated C-H); 2874, 2924 and 2947 cm⁻¹ s (ν_s saturated C-H); 1604 cm⁻¹, m (ν_s Ph ring); 1207, 1400 cm⁻¹, s (ν_s C-O-H); and 1134 cm⁻¹, vs (ν_s C-O-C). ¹H-NMR (chloroform-d): δ (ppm) = 5.37 (t), 5.56 (t) (Ph-C(CH₂)O-); 5.06 (t) (-CH(Ph)CH₂OH); 4.22 (t), 4.41 (t) (-OCH(Ph)CH₂OH); 3.8 (m) (-OCH(Ph)CH₂OH). MS(CI): m/e = 241(61.3%, P+1), 223(16.5%, P+1-H₂O), 149(100%), and 121(46.9%, PhC(CH₂)O fragment). One of

the products that is insoluble in cyclohexane is probably a ring opened oligomer of styrene oxide, which could be washed from the immobilized catalyst with diethyl ether. The catalyst was used in five successive cycles, but the cocatalyst methyl iodide was added only before the first.

2.5. Dimerization of styrene oxide using CTAB- $[Rh(CO)_2I_2]^-$ as homogeneous catalyst

Cetyltrimethylammonium bromide (CTAB) (1.86 g, 5 mmol) and $RhCl_3 \cdot 3H_2O$ (50 mg, 0.19 mmol) were dissolved in 45 ml water and the solution introduced in a Parr high-pressure reactor. Then styrene oxide (7.2 g, 60 mmol) and 1 ml of methyl iodide were added to the aqueous solution. The reaction conditions were the same as in section 2.4. After reaction, cyclohexane (40 ml) was introduced, and a three-phase system appeared: a cyclohexane layer; a deep brown organic layer containing rhodium carbonyl complex; and an aqueous layer. In order to remove the catalyst, the organic layers were passed through a silica gel column followed by elution with chloroform (40 ml). The catalyst was adsorbed in the column, while the products were washed out. An oil (2.4 g) remained after the evaporation of the eluants.

2.6. Carbonylation of styrene oxide using PDVB (PEVAC)- $[Co(CO)_4]^-$ as a heterogeneous catalyst

PDVB(PEVAC) powder (1.5 g) was dispersed in 45 ml water in the Parr high-pressure reactor. Purple-black $CoCO_3$ powder (0.3 g), methyl iodide (1 ml) and styrene oxide (8.4 g, 70 mmol) were subsequently introduced. The system was purged three times at room temperature with CO (5–10 psi) with slow stirring. Then, CO was introduced until a pressure of 200 psi was achieved and the reaction was conducted with stirring at 95–98°C for 16 h. After reaction, about 40 ml cyclohexane was added, followed by vigorous stirring for a few minutes to extract the organic compounds. The system was filtered to separate

the yellowish immobilized polymer catalyst from the liquid phases, which were separated, and the aqueous phase was extracted twice with diethyl ether (2 × 20 ml). The ether extract was added to the cyclohexane solution. Needle-like yellow crystals grew during the overnight evaporation of the solvents in a fume hood at ambient temperature. The crystals were purified twice by dissolving them in 15 ml diethyl ether and then precipitating with a large amount of petroleum ether. Finally 6.6 g of white solid was obtained. FT-IR, 1H -NMR and MS data indicated that the product was 2,5-dihydro-2-oxo-3-hydroxy-4-phenylfuran (Scheme 1). FT-IR spectrum (chloroform): 3300–3600 cm^{-1} , s (ν_s OH); 2831 cm^{-1} , s (ν_s saturated CH); 1716 cm^{-1} , w, 1693 cm^{-1} , s (ν_s C=O); 1099 and 1319 cm^{-1} , s (ν_s C–O–C). 1H -NMR (chloroform-d): δ (ppm) = 3.74 (s, –OH); 4.77 (s), 4.79 (d) (–CH₂O–); and 7.32 (s, Ph). MS(CI): m/e = 177 (3%, P + 1), 159 (3%, P + 1 – H₂O), 143 (4%), 121 (100%, styrene oxide fragment) and 105 (21%, styrene fragment). The immobilized catalyst was used in five successive cycles; the cocatalyst methyl iodide was introduced only before the first cycle.

3. Results and discussion

3.1. Porous nutshell polymer particles as molecular reservoirs

A method for the generation of porous nutshell particles, based on a two-step concentrated emulsion polymerization, was proposed in a previous paper [14]. In these particles submicron crosslinked polydivinylbenzene domains constitute a porous shell surrounding a 'void' filled with polyvinylbenzyl chloride (PVBC) coils. The two steps of the procedure were: 1) a concentrated emulsion in water of a solution of vinylbenzyl chloride in a mixture of toluene and octane was polymerized. The resulting polar PVBC, was swollen by toluene (the more polar solvent), and a nucleus was thus generated surrounded by

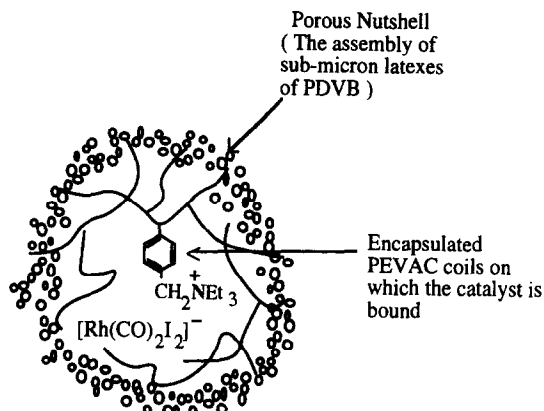


Fig. 1. Cross-section of the nutshell catalyst.

octane (nonpolar), which is a nonsolvent for PVBC; 2) Divinylbenzene (DVB), which mixes with octane, was introduced into the emulsion after the polymerization of VBC. The polymerization of DVB, initiated by the AIBN molecules already present in the toluene-swollen PVBC nuclei, generated a highly porous wall. The pendant benzylchloride groups of the encapsulated PVBC chains can be converted to a variety of organic functional groups, such as ligands, quaternary onium salts, crown ethers and other reactive intermediates. The quaternary triethylbenzylammonium chloride was selected as the target functional group for binding transition metal carbonyl anions (Figs. 11 and 1).

PDVB(PVBC) was converted via quaternization to PDVB(PEVAC). The porous structure of the latter particles was examined with SEM (Fig. 2). The FT-IR spectra of PDVB(PVBC) and PDVB(PEVAC) are presented in Fig. 3, and the elemental analyses for PDVB(PEVAC) and the immobilized catalysts in Table 1. The absorption bands at 796 and 709 cm^{-1} (Fig. 3a) correspond to the groups $\text{Bzl}-\text{Cl}$ which are encapsulated by a porous PDVB shell; those at 1442 , 1365 , 1221 , 1093 , 904 and 711 cm^{-1} (Fig. 3b) correspond to the pendant groups $\text{Et}_3\text{BzlN}^+\text{Cl}^-$. The latter compound was formed via nucleophilic substitution of Cl by Et_3N .

Even in the presence of the hydrophobic shell (PDVB), the PDVB(PEVAC) particles remained dispersed in the water phase. Probably some tails of the poly(triethyl vinylbenzylam-

monium chloride) protrude through the porous polydivinylbenzene. Their charges generate electrostatic repulsion among the particles, and this ensures some stability of the dispersion in water. Because the particles are about $10\ \mu$ size, some sedimentation also occurred, which was avoided by mechanical stirring. The existence of electrostatic repulsion was verified by shielding the electric field by the addition of an electrolyte, $(\text{NH}_4)_2\text{S}_2\text{O}_8$, to the aqueous dispersion. At a concentration of $0.5\ \text{M}$, the sedimentation was tremendously accelerated. It is likely that water molecules pass through the lipophilic porous PDVB shell and swell the hydrophilic encapsulated PEVAC chains forming a micro-water pool.

3.2. Double carbonylation of styrene oxide catalyzed by PDVB(PEVAC) immobilized cobalt carbonyl complexes

The homogeneous catalytic synthesis of 2,5-dihydro-2-oxo-3-hydroxy-4-phenylfuran, via the double carbonylation of styrene oxide, was pre-

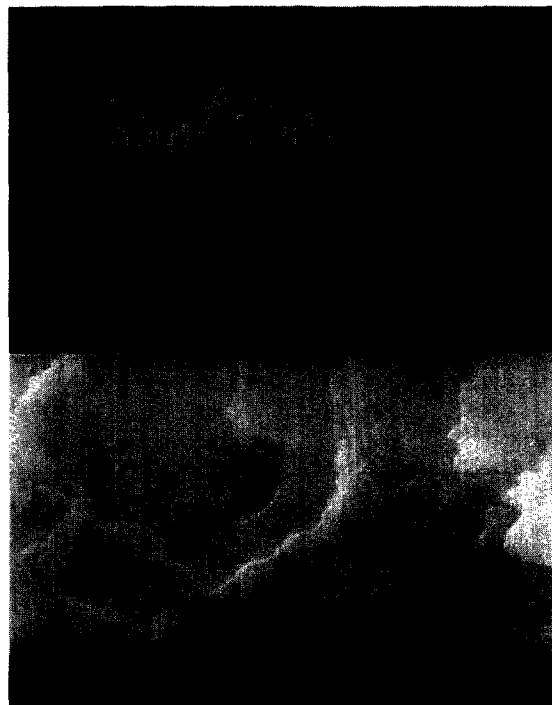


Fig. 2. Scanning electron microscopy images of the porous nutshell PDVB(PEVAC) particle.

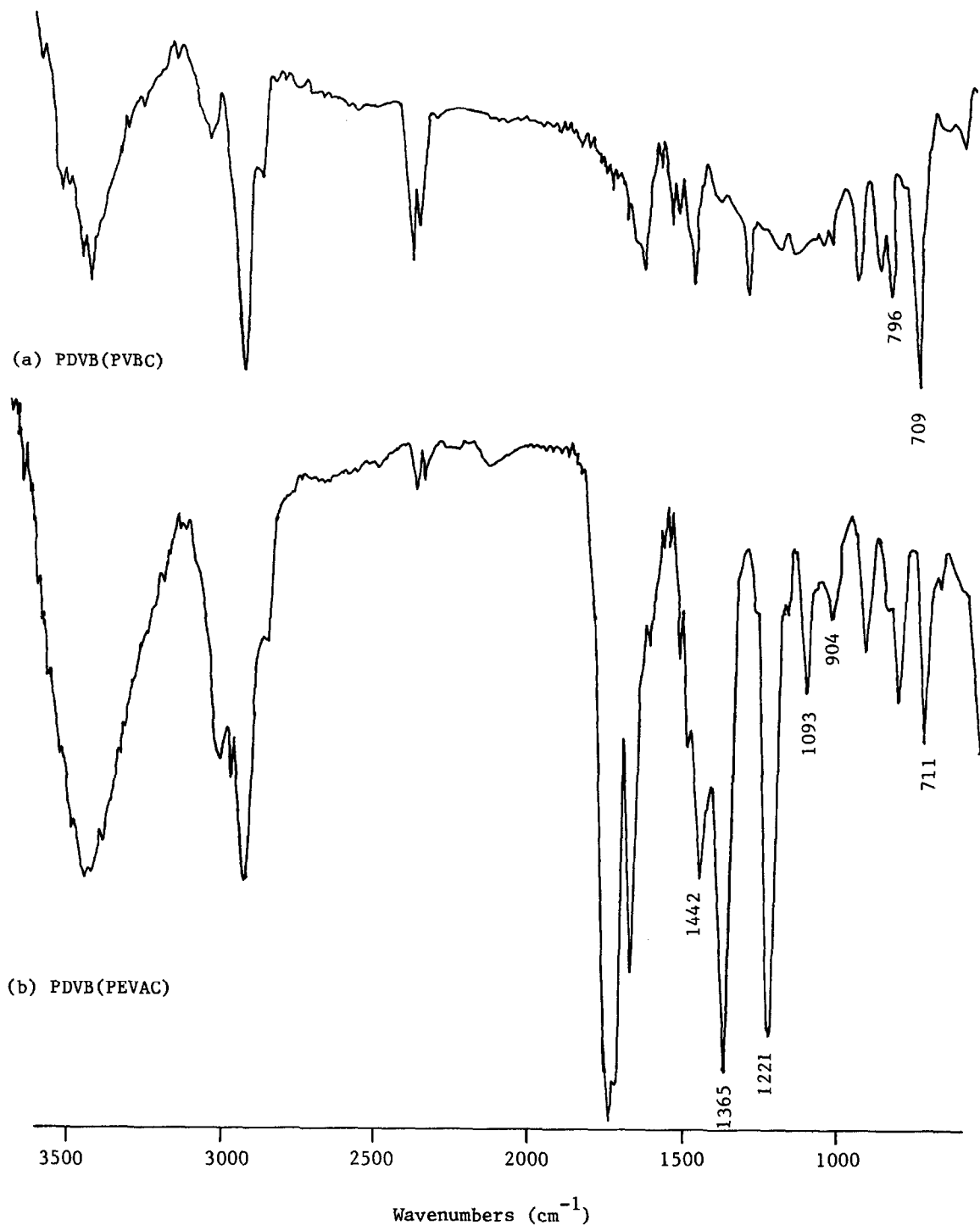


Fig. 3. FT-IR spectra of (a) PDVB(PVBC) and (b) PDVB(PEVAC).

viously [15] achieved in the presence of cobalt carbonyl and cetyltrimethylammonium bromide (CTAB). This product can be employed as a new

monomer in ring opening polymerization. Immobilization of the homogeneous catalysts by load-

Table 1

The compositions of the molecular reservoir PDVB(PEVAC) and the immobilized catalysts

Molecular reservoir and catalysts	N (mmol/g)	Fresh ^b (mmol/g)			Used ^c (mmol/g)		
		N	Co	Rh	N	Co	Rh
PDVB(PEVAC) ^a	1.35						
PDVB(PEVAC)-[Rh(CO) ₂ I ₂] ⁻		1.11		0.16	0.82		0.15
PDVB(PEVAC)-[Co(CO) ₄] ⁻			0.60			0.43	

^a PDVB(PEVAC) was prepared by the quaternization of PDVB(PVBC). The latter particles were prepared by the concentrated emulsion polymerization (for details see Section 2.3).

^b The catalyst was prepared by stirring a mixture of 1.5 g PDVB(PEVAC) and CH₃I (1 ml) with an aqueous solution of RhCl₃·3H₂O (60 mg) in 45 ml water or with a suspension of CoCO₃ (0.3 g) in 45 ml water under 200 psi CO at 95°C for 2 h.

^c The catalyst was analysed after 5 successive cycles.

ing on PDVB(PEVAC) improves catalysis in two ways:

(1) In the aqueous–organic two-phase homogeneous catalytic system, the CTAB cation plays the role of a vehicle which carries the catalytically active tetracarbonyl anion from the aqueous phase into the organic phase, where the styrene oxide and the cocatalyst CH₃I are present. In the homogeneous case, the reaction did not occur in the absence of sodium hydroxide [15]. It did occur

without sodium hydroxide, however, when the molecular reservoir PDVB(PEVAC) was used. The probable reason is that in the two-phase homogeneous system, the concentration of OH⁻ in the aqueous phase affects the ability of the CTAB cation to carry the Co(CO)₄⁻ anion into the organic phase. In the present heterogeneous case, the immobilized catalyst PDVB(PEVAC)-Co(CO)₄⁻ is dispersed in water, and the styrene oxide molecules must be adsorbed from their dis-

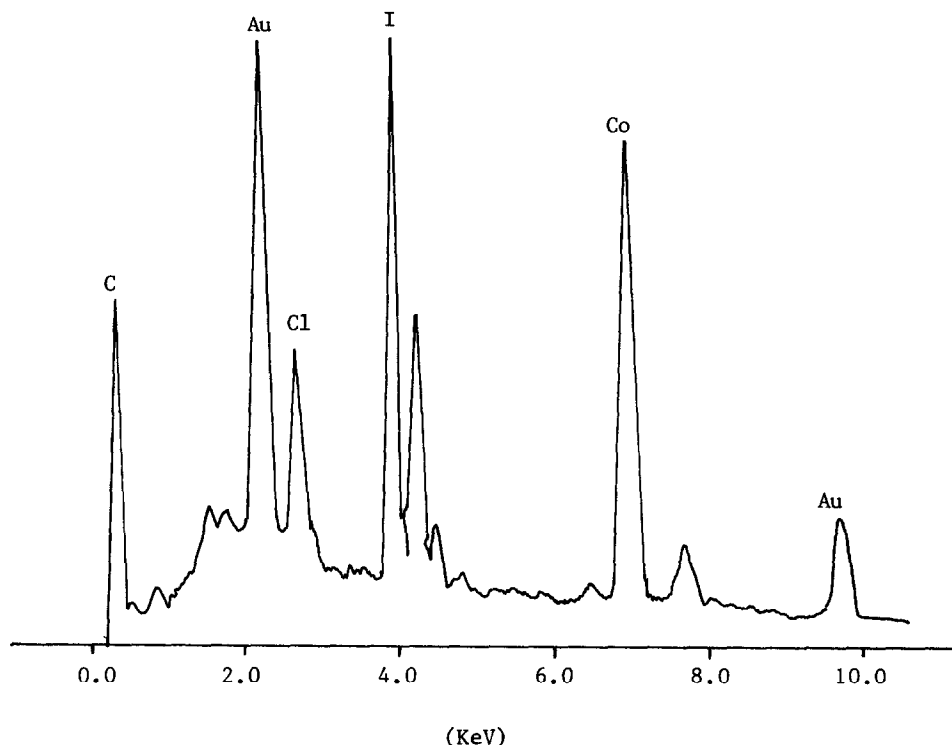


Fig. 4. Energy dispersive spectra of the PDVB(PEVAC) supported Co catalyst after five cycles.

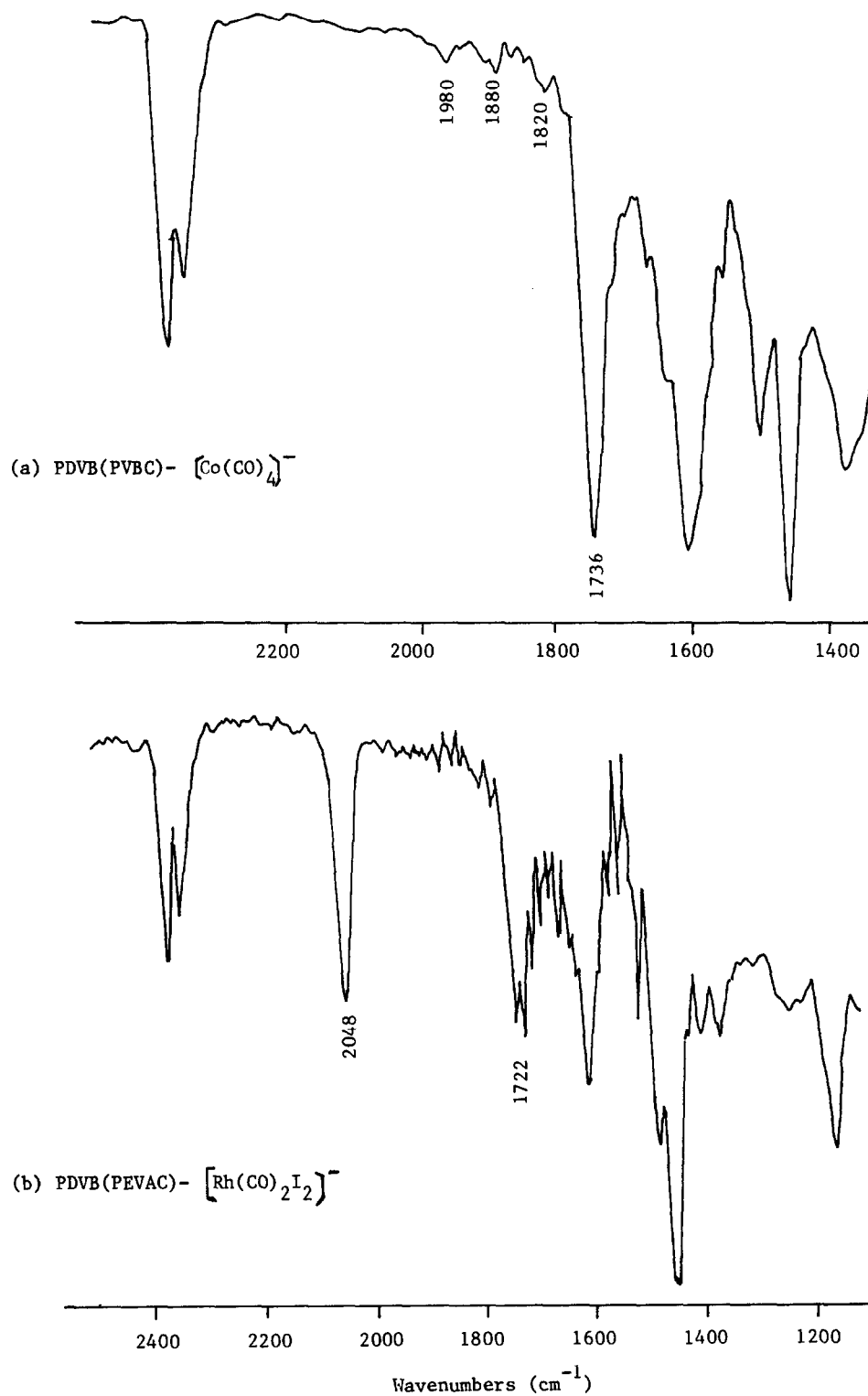


Fig. 5. FT-IR of (a) the PDVB(PEVAC) supported Co catalyst after five cycles, and (b) the PDVB(PEVAC) supported Rh catalyst after five cycles.

Table 2
Yield of 2,5-dihydro-2-oxo-3-hydroxy-4-phenylfuran after each of five successive cycles of the double carbonylation of styrene oxide

1st (16 h)	2nd (16 h)	3rd (16 h)	4th (6 h)	5th (12 h)
66%	64%	76%	57%	70%

persed droplets in the lipophilic porous nutshell PDVB of the molecular reservoir catalyst PDVB(PEVAC)-Co(CO)₄⁻. For this reason, no organic solvent was used, to maintain the high concentration of the styrene oxide in the porous shell of the molecular reservoir.

(2) Iodine containing compounds, in most cases methyl iodide, are used as cocatalysts for the catalytic carbonylation of alcohols and epoxides. Because they are expensive and corrosive, their recycling constitutes an important goal. In the molecular reservoir based catalytic system, methyl iodide was introduced only in the first cycle. The EDS spectrum of the immobilized catalyst PDVB(PEVAC)-[MeCOCo(CO)₄] after five cycles exhibits both the iodine and cobalt peaks (Fig. 4). The FT-IR spectrum of the immobilized catalyst (Fig. 5-a) exhibits carbonyl absorption bands at 1736 cm⁻¹ (s), 1820 cm⁻¹ (w), 1880 cm⁻¹ (w) and 1980 cm⁻¹ (w). The absorption band at 1736 cm⁻¹ can be assigned to the ν_{C=O} of the coordinated acetyl group MeCO-

The latter group is generated via the oxidative

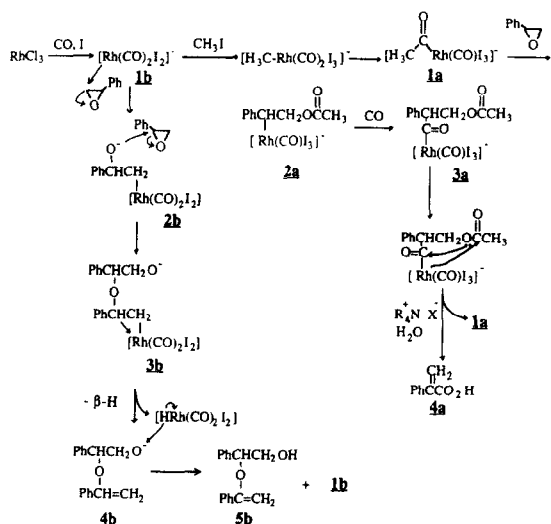


Fig. 6. Schematic presentation of two possible reaction pathways.

addition of CH₃I to [Co(CO)₄]⁻ and insertion of the carbonyl into the Me-Co bond. The acetyl group functions as acceptor for the β-ethoxy anion generated when the [Co(CO)₄]⁻ anion attacks the α-carbon of styrene oxide, and is returned to the cobalt after one catalytic cycle [15]. The other three carbonyl absorptions are very weak because of a very low content of carbonyl ligands, since their coordination to cobalt becomes unstable when exposed to air [16]. However, they are regenerated under a CO atmosphere [17]. The elemental analysis of the catalyst indicated that 72% of the initial cobalt was still present after 5 cycles (Table 1).

The HPLC analysis of the reaction products after each of the cycles indicated that only a very small amount of styrene oxide remained unconverted. The yields of the main product, 2,5-dihydro-2-oxo-3-hydroxy-4-phenylfuran, at the end of each of the five cycles, are given in Table 2.

3.3. Dimerization of styrene oxide catalyzed by the [Rh(CO)₂I₂]⁻ complex immobilized on PDVB(PEVAC)

The homogeneous commercial synthesis of acetic acid is performed by reacting methanol with CO at about 180°C and 30–40 atm in the presence of 10⁻³ M Rh [4]. The active rhodium catalyst, [Rh(CO)₂I₂]⁻, is generated by the reaction between RhCl₃·3H₂O and methyl iodide in the presence of CO. The above Rh catalyst is also effective in the conversion of the higher alcohols to the homologous carboxylic acids. For this reason, our initial attempt was to convert *sec*-phenethyl alcohol to 2-phenylpropanoic acid by employing the immobilized catalyst PDVB(PEVAC)-[Rh(CO)₂I₂]⁻. This conversion did not, however, occur. Instead, β-hydrogen elimination from the 2-phenethyl group gave styrene, which underwent subsequent polymerization. Synthesis of α-phenylacrylic acid (4a) by carbonylation of styrene oxide was attempted (Fig. 6). Unexpectedly, the main product was 2-phenyl-2-(α-styryloxy)ethanol (5b) rather than α-phenylacrylic acid.

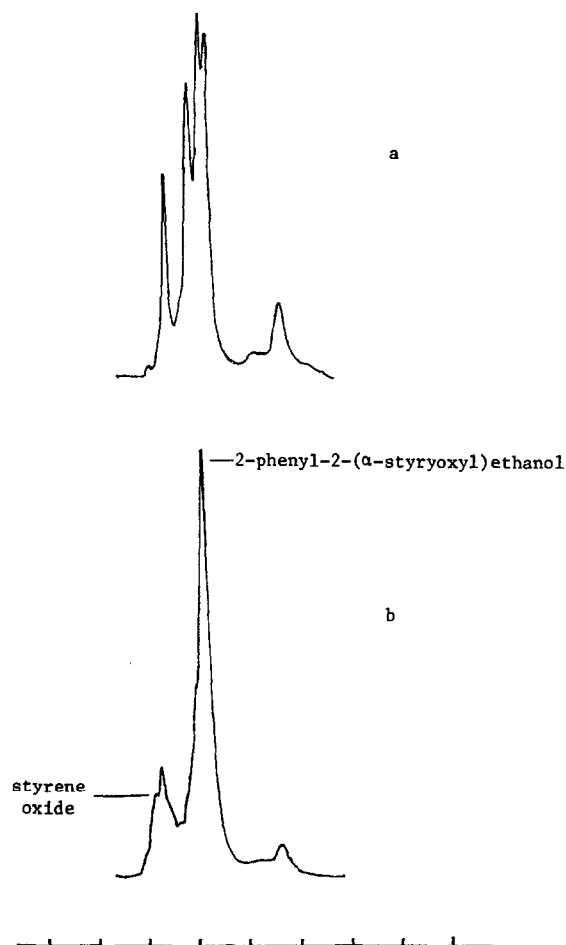


Fig. 7. HPLC analysis of the products of (a) dimerization of styrene oxide using the homogeneous $[\text{Rh}(\text{CO})_2\text{I}_2]^-$ -CTAB catalyst; and (b) using the heterogeneous PDVB(PEVAC)- $[\text{Rh}(\text{CO})_2\text{I}_2]^-$ catalyst.

It is likely that after the formation of the intermediate **2b**, via the electrophilic substitution of styrene oxide in **1b**, electrophilic attack on **2b** by another styrene oxide molecule generates the intermediate **3b**. The rapid elimination of β -H from the alkyl group of **3b** generates the alkyoxyl anion **4b**, which abstracting a proton from the rhodium hydride transforms into **5b** (2-phenyl-2-

Table 3

Yield of 2-phenyl-2-(α -styryloxy)ethanol after each of five successive cycles of the dimerization of styrene oxide

1st	2nd	3rd	4th	5th
37%	52%	58%	58%	55%

(α -styryloxy)ethanol). The active catalytic species **1b** is thus regenerated. It seems that the intermediate **1a** has a more crowded coordination sphere and hence is a less reactive intermediate than **1b**. As a result, the intermediate **2b** is generated instead of **2a**.

For comparison purposes, a homogeneous catalytic system, consisting of RhCl_3 , CTAB and MeI was also used under the conditions employed for the immobilized system. The HPLC diagrams (Fig. 7) show that the selectivity for 2-phenyl-2-(α -styryloxy)ethanol is much lower in the homogeneous case than in the heterogeneous one. Very likely this occurs because of the agglomeration of rhodium carbonyl complexes $[\text{Rh}(\text{CO})_2\text{I}_2]^-$ in the homogeneous case.

The immobilized catalyst PDVB(PEVAC)- $[\text{Rh}(\text{CO})_2\text{I}_2]^-$ was used in five successive cycles (Table 3). After the five cycles, the elemental analysis of the catalyst indicated that 94% of the initial rhodium was still present (Table 1). The FT-IR spectrum (Fig. 5-b) of the catalyst after 5 cycles presents a strong carbonyl ligand absorption band at 2048 cm^{-1} and a strong carbonyl absorption of the acetyl ligand at 1722 cm^{-1} . This indicates that **1a** is more stable chemically in the reservoir than **1b**.

4. Conclusion

A two-step concentrated emulsion polymerization procedure was employed to encapsulate poly(vinylbenzyl chloride) [PVBC] coils in porous poly(divinylbenzene) [PDVB] nutshells. After quaternization of the PVBC, a molecular reservoir [denoted PDVB(PEVAC)] was generated. The hydrophilic PEVAC cation chains constitute the anchors binding the metal carbonyl anions $[\text{Co}(\text{CO})_4]^-$ or $[\text{Rh}(\text{CO})_2\text{I}_2]^-$ to the interior of the reservoir. The porous lipophilic PDVB shells function as adsorbents for the styrene oxide molecules. 2,5-dihydro-2-oxo-3-hydroxy-4-phenylfuran was obtained as the main product when PDVB(PEVAC)- $\text{Co}(\text{CO})_4^-$ was employed in the presence of CO. After five cycles,

72% of the initial Co was still present in the reservoir. When PDVB(PEVAC)-[Rh(CO)₂I₂]⁻ was employed, 2-phenyl-2-(α -styryloxy)ethanol was unexpectedly obtained as the main product. After five cycles, 94% of the initial Rh was still present in the reservoir.

Acknowledgements

This work was supported by the National Science Foundation. We thank the Editor for helpful suggestions.

References

- [1] (a) H. Joseph, C & EN, May 21 (1990) 30; (b) J.K. Stille, in B.M. Trost and I. Fleming (Eds), *Comprehensive Organic Synthesis*, Vol. 4, Pergamon Press, Oxford, 1991, Chap. 4, p. 913; (c) H. Alper, *Aldrichimica*, 24 (1) (1991) 3.
- [2] H.M. Colquhoun, D.J. Thompson and M.V. Twigg, *Carbonylation Direct Synthesis of Carbonyl Compounds*, Plenum, New York, 1991.
- [3] K. Weissmehl and H.J. Arpe, *Industrial Organic Chemistry*, Verlag Chemie, Weinheim, 1978, p. 254.
- [4] J.F. Roth, J.H. Craddock, A. Hershman and F.E. Paulik, *Chemtech.*, 1 (1971) 600.
- [5] a. L. Cassor, *Chem. Ind. (Milan)*, 67 (1985) 256; b. H. Maekawa, S. Takahashi and H. Urata, *J. Org. Chem.*, 56 (1991) 4320; c. F. Mathe, Y. Castanet, A. Mortreux and F. Petit, *Tetrahedron Lett.*, 32 (1991) 3989.
- [6] G. Cavinato and L. Toniolo, *J. Organomet. Chem.*, 398 (1990) 187.
- [7] D. Bingham, B. Hudson, D. Webster and P.B. Wells, *J. Chem. Soc., Dalton Trans.*, (1974) 1521.
- [8] (a) G. Jenner, E.M. Nahmed and S. Libskonrath, *J. Mol. Catal.*, 64 (1991) 4917; (b) J.D. Gargulak and W.L. Gladfelder, *J. Am. Chem. Soc.*, 116 (1994) 3792.
- [9] O.P. Vig, *J. Ind. Chem. Soc.*, 59 (1982) 609.
- [10] G.W. Parshall and S.D. Ittel, *Homogeneous Catalysis – The Applications and Chemistry of Catalysis by Soluble Transition Metal Complexes*, 2nd Ed., John Wiley and Sons, Inc., New York, 1992.
- [11] (a) P. Hodge, *Polymers as Chemical Reagents*, in J.I. Kroschwitz (Ex. Ed.), *Encyclopedia of Polymer Science and Engineering*, 2nd Ed., John Wiley and Sons, New York, 1988; (b) A.D. Pomogailo, *Russ. Chem. Rev.*, 61 (1992) 133; (c) C.U. Pittman, Jr. and Q. Ng, *J. Organomet. Chem.*, 153 (1978) 85.
- [12] (a) W.M.H. Sachtler and Z.-C. Zhang, *Adv. Catal.*, 39 (1993) 129; (b) B.C. Gates L.V. Interrante, L.A. Casper, A.B. Ellis (Eds.), in *Materials Chemistry*, American Chemical Society, Washington, DC, 1995, Chap. 12, p. 301.
- [13] (a) E. Ruckenstein and L. Hong, *Chemistry of Materials*, 4 (1) (1992) 122; (b) L. Hong and E. Ruckenstein, *React. Polym.*, 16 (1991/1992) 181; (c) L. Hong and E. Ruckenstein, *J. Chem. Soc., Chem. Commun.*, (1993) 1486; (d) M.J. Sundell and J.H. Näsman, *Chemtech.*, December (1993) 16.
- [14] E. Ruckenstein, L. Hong, *Chem. Mater.*, 4 (1992) 1032.
- [15] H. Alper, H. Arzoumanian, J.-F. Petrigiani and M. Saldana-Maldonado *J. Chem. Soc., Chem. Commun.*, (1985) 340.
- [16] W.F. Edgell and J. Lyford, IV, *J. Chem. Phys.*, 52 (1970) 4329.
- [17] F.S. Wagner and H.W. Richardson, in J.I. Kroschwitz (Ex. Ed.) and M. Howe-Grant (Ed.), *Encyclopedia of Chemical Technology*, 4th Ed., John Wiley and Sons, New York, 1993, Vol. 5, p. 123 and Vol.6, p. 778.