

1,3-Butadiene telomerization with methanol catalyzed by heterogenized palladium(II) complexes anchored to polymer-bound bis(diphenylphosphino)methane moieties

Federica Benvenuti ^a, Carlo Carlini ^{a,*}, Mario Marchionna ^b, Renata Patrini ^b,
Anna Maria Raspolli Galletti ^a, Glauco Sbrana ^a

^a *Dipartimento di Chimica e Chimica Industriale, University of Pisa, Via Risorgimento 35, I-56126 Pisa, Italy*

^b *SNAMPROGETTI, Via Maritano 26, I-20097 San Donato Milanese, Italy*

Received 4 March 1998; accepted 5 June 1998

Abstract

The telomerization of 1,3-butadiene with methanol in the presence of heterogenized palladium(II) catalysts, obtained by anchoring the metal on both a styrene/divinylbenzene macroporous resin and a linear poly(styrene) functionalized with bis(diphenylphosphino)methane moieties, is reported. In particular, the activity and selectivity to telomers of the above catalytic systems is compared with the corresponding homogeneous counterpart and with those previously obtained with analogous heterogenized systems via polymer-bound 1,3-bis(diphenylphosphino)propane moieties. The effect of a methoxide promoter is also studied. Finally, the performances and metal leaching in solution of the above heterogenized catalysts are checked after several reaction cycles in order to verify their real heterogeneous character. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Telomerization; 1,3-Butadiene; Methanol; Palladium(II) complexes; Phosphinated styrene/divinylbenzene resins; Heterogenized catalysts

1. Introduction

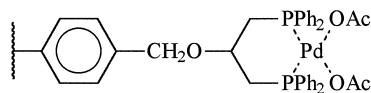
The anchorage of transition metal complexes to polymeric matrices represents a powerful tool for obtaining heterogenized catalysts which may combine the specific properties of both homogeneous and heterogeneous systems, the former

being characterized by high activity, reproducibility and modulable selectivity, the latter by higher stability, easy separability from the reaction products and recyclability [1–3].

In this context, we reported [4] very recently the use of heterogenized palladium(0) and palladium(II) catalysts for 1,3-butadiene telomerization with methanol, obtained by anchoring the metal species to chelating 1,3-bis(diphenylphosphino)propane (DPPP) moieties linked to both

* Corresponding author. Fax: +39-50-918260; E-mail: carlini@dcci.unipi.it

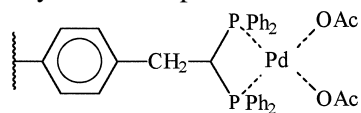
styrene/divinylbenzene crosslinked resins and to linear poly(styrene), the structure of the metal coordinated units being represented below.



The above reaction was chosen for the interest to produce selectively, according to Scheme 1, the linear telomers which after hydrogenation may be used as a component for diesel fuels owing to their excellent cetane number and cold flow properties [5]. Moreover, with the aim to design catalysts really working in the heterogeneous phase, telomerization reaction appeared as one of the most severe tests to verify the strength of the linkage between the metal and the anchoring chelating moiety, due to the competitive presence of a large excess of 1,3-butadiene [6].

Indeed, the above heterogenized catalysts were reported [4] to display activity and selectivity similar to those found for the corresponding homogeneous counterpart and to work as real heterogeneous systems, no appreciable metal release into solution being observed. However, taking into account that homogeneous palladium complexes based on bis(diphenylphosphino)methane were recently found to display a significantly higher activity in the 1,3-butadiene telomerization with alcohols, as compared with the corresponding systems obtained from DPPP [7], novel heterogenized palladium(II) complexes were synthesized [8] by anchoring the metal species to bis(diphenylphosphino)methane chelating moieties bound to either a crosslinked styrene/divinylbenzene resin or a linear poly(styrene). The proposed structure [8] of the palladium(II) complexes coordinated

to the phosphinated styrene co-units in the above polymeric systems is represented below.



Therefore, this paper is devoted to the investigation of the activity and selectivity of the above heterogenized catalysts in 1,3-butadiene telomerization with methanol, by comparing their performances with those previously obtained with the heterogenized polymer-bound DPPP analogous systems as well as with the corresponding homogeneous counterpart. Particular emphasis will be also devoted to the study of metal leaching into solution during the catalytic cycles, in order to verify the real heterogeneous character of these palladium catalysts.

2. Experimental

2.1. Materials

All manipulations as well as catalytic reactions were carried out under dry purified argon or nitrogen using standard Schlenk techniques.

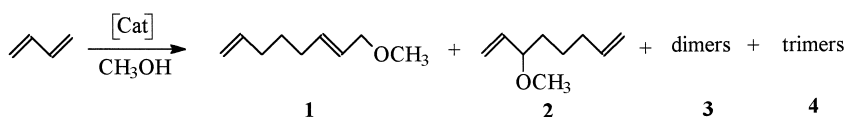
All solvents, after drying, were stored on molecular sieves (4 Å), under dry inert atmosphere.

Tetrahydrofuran (THF) (Carlo Erba) was refluxed on Na/K alloy and distilled on LiAlH₄.

Toluene (Baker) and dioxane (Carlo Erba) were refluxed and distilled on sodium.

n-Hexane (Merck) was refluxed and distilled on Na/K alloy.

Anhydrous methanol was obtained by refluxing the commercial product (Baker) over Mg/I₂ and stored on molecular sieves (4 Å).



Scheme 1.

1,3-Butadiene (99%) (Rivoira) was flash-distilled prior to use in order to avoid contamination from 4-vinyl-cyclohexene and peroxides.

Bis(diphenylphosphino)methane (DPPM) (97%, Aldrich) was used as received and stored under inert atmosphere.

Sodium methoxide (95%, Aldrich) was dried under vacuum at 50°C and stored under dry inert atmosphere.

Palladium bis-(di-benzylidene-acetone) [Pd(dba)₂] was prepared as previously described [9].

Palladium(II) acetate [Pd(OAc)₂] (Aldrich) was used as received and stored under anhydrous atmosphere.

The heterogenized Dow–DPPM–Pd(OAc)₂ catalyst precursor (2.83 wt.% of Pd, corresponding to 0.266 meq Pd/g of resin) was obtained, as previously reported [8], by reacting Pd(OAc)₂ with a macroporous crosslinked styrene (St)/divinylbenzene (DVB) resin (Dow-B) (specific surface area = 45 m²/g) containing 4.5 mol% of DVB co-units and functionalized with bis(diphenylphosphino)methane (DPPM) moieties (3.5 mol% of St-DPPM co-units).

The heterogenized Pst–DPPM–Pd(OAc)₂ catalyst precursor (0.75 wt.% of Pd, corresponding to 0.071 meq Pd/g of polymer) was prepared as previously described [8], by reacting Pd(OAc)₂ with a linear poly(styrene) (Aldrich) (*M_w* = 45,000 Da) functionalized with DPPM moieties (0.7 mol% of St-DPPM co-units).

2.2. Catalytic experiments and analyses

Catalytic experiments were carried out in a 150-ml mechanically stirred stainless steel autoclave, equipped with an inner glass beaker, a substrate inlet vessel and a sampling valve. In a typical procedure, the desired amount of methanol, palladium catalyst, benzene (as internal standard for GC analysis) and eventually the solvent, phosphine ligand and sodium methoxide promoter were introduced under dry argon into the nitrogen purged autoclave. Then, 1,3-butadiene was charged and the system pressur-

ized with nitrogen to 3 MPa. The autoclave was heated to the desired temperature in a thermostatted oil bath. Product samples were periodically removed via the liquid sampling valve, collected in pre-cooled capped vials and immediately analysed by GC. At the end of the reaction the autoclave was cooled at room temperature and, after removing unreacted 1,3-butadiene, the products analysed. In recycle experiments of the catalyst, the liquid solution of the products, after catalyst sedimentation, was removed under dry argon and fresh methanol, 1,3-butadiene and eventually sodium methoxide were added in the proper quantities. When the products solution was recycled, the reaction mixture was analysed and removed under dry argon from the autoclave; then the catalyst was settled, the solution, including the unreacted methanol, was again transferred under argon into the autoclave and fresh 1,3-butadiene was charged in the appropriate molar ratio with methanol.

Quantitative analyses of telomerization products were performed by a SIGMA 3B Perkin-Elmer gas chromatograph, equipped with a P.C. PE NELSON integrator, a flame ionization detector and a 25-m HP5 capillary column (5% crosslinked methyl-phenyl-silicone). The identification of the telomerization products was carried out by GC/MS and NMR analyses.

The content of palladium released in the liquid reaction medium during the catalytic cycles was determined by UV–VIS spectrophotometric analysis at 408 nm, according to the literature [10]. The calibration curve was obtained with five standard solutions of sodium tetraiodopalladate at different concentration.

2.3. Physicochemical measurements

Elemental analyses on catalyst samples were carried out at the Analytical Laboratory of Pharmacy Faculty of the University of Pisa.

GC/MS spectra of the telomerization products were performed by a Hewlett-Packard 5995 A spectrometer.

UV–VIS analyses were accomplished by using a Pharmacy-NOVASPEC II unibeam spectrophotometer.

³¹P-NMR spectra of catalyst samples in the solid state for the quantitative determination of P^(V) and P^(III) were performed on a AMX 300 BRUKER spectrometer, equipped with a CP-MAS apparatus working at 8000 Hz.

3. Results and discussion

3.1. 1,3-Butadiene telomerization with methanol catalyzed by Dow–DPPM–Pd(OAc)₂ in the absence of alkaline alkoxides

As reported in Table 1, Dow–DPPM–Pd(OAc)₂ displays (run 3) a much lower activity as compared with that observed in the presence of the corresponding homogeneous catalyst prepared in situ from Pd(OAc)₂ and DPPM with a P/Pd molar ratio equal to 2 (run 2). Indeed, the latter system gives rise to a 3-fold 1,3-butadiene conversion with a much shorter reaction time (4 h against 18 h). Moreover, the homogeneous system shows a higher selectivity to telomers and particularly towards the linear

telomers *cis*- and *trans*-1-methoxy-2,7-octadiene (**1**). The lower regioselectivity observed in the reaction catalyzed by Dow–DPPM–Pd(OAc)₂ (run 3) may be connected with the detection of a small amount of butenyl ethers, analogously to what previously found in the presence of Pd(II) catalyst precursors without the use of alkoxide promoters [11,12]. Indeed, considering that the formation of 3-methoxy-1-butene is favoured with respect to the linear isomer [11], the conversion of butenyl ethers in telomers increases the relative amount of 3-methoxy-1,7-octadiene (**2**). However, Dow–DPPM–Pd(OAc)₂ shows a much higher activity and also selectivity with respect to those reported [4] for the corresponding heterogenized system anchored to a Dow resin functionalized with DPPP moieties [Dow–DPPP–Pd(OAc)₂], under similar conditions (run 1), where dimers were almost quantitatively produced. The above results confirm what had previously been observed for the corresponding homogeneous catalysts [7], i.e., Pd(II) complexes with diphosphine moieties which are able to give, as DPPP, five- or six-membered metallacycles result too stable for promoting high catalytic activity in

Table 1

1,3-Butadiene telomerization with methanol catalyzed by different heterogenized palladium(II) complexes anchored to polymer-bound diphenylphosphine and by the homogeneous analog^a

Run	Catalyst precursor	C ₄ H ₆ /Pd (mol/mol)	C ₄ H ₆ conversion (%)	Reaction conditions		Products ^b (mol%)			R ^c (%)
				time (h)	T (°C)	1 ^d	2 ^e	3 ^f	
1	Dow–DPPP–Pd(OAc) ₂ ^g	6500	1.7	18	60	0.7	0.3	99.0	70.0
2	Pd(OAc) ₂ /DPPM	2000	96.0	4	60	88.6	6.5	4.8	93.2
3	Dow–DPPM–Pd(OAc) ₂	2000	32.8	18	60	74.7	13.7	11.5	84.5
4	2nd cycle	2000	18.4	18	60	76.1	16.2	7.7	82.4
5	3rd cycle	2000	18.2	18	60	75.5	16.0	8.5	82.5
6	Dow–DPPM–Pd(OAc) ₂	2000	48.8	18	80	68.1	15.3	16.6	81.7
7	2nd cycle	2000	33.5	18	80	70.3	14.9	14.8	82.5
8	3rd cycle	2000	27.7	18	80	70.6	14.7	14.7	82.8
9	4th cycle	2000	17.2	18	80	64.9	14.1	21.0	82.2
10	5th cycle	2000	16.5	18	80	70.2	12.4	17.4	85.0

^aPd: 0.05 mmol; P/Pd and MeOH/C₄H₆ = 2 and 1.5 mol/mol, respectively; *n*-hexane: 20 ml; P_{N₂} = 3 MPa.

^bWhen **1** + **2** + **3** < 100, trimers are also present to some extent.

^cRegioselectivity to the linear telomers **1**, expressed as [**1**/(**1** + **2**)] × 100.

^d*Cis*- and *trans*-1-methoxy-2,7-octadiene.

^e3-Methoxy-1,7-octadiene.

^fMainly 1,3,7-octatriene and 4-vinyl-cyclohexene. In run 3 a small amount of butenyl ethers is also present.

^gRef. [4]; in the absence of *n*-hexane.

the telomerization reaction, at least in the absence of an alkoxide promoter.

In order to check if Dow–DPPM–Pd(OAc)₂ really worked as a heterogeneous system, the solid catalyst, after its use in run 3 was recycled several times under the same experimental conditions, i.e., by adding fresh *n*-hexane, 1,3-butadiene and methanol to reach the pristine relative amounts. As reported in Table 1, the activity of the catalyst decreases on going from the 1st cycle (run 3) to the subsequent 2nd and 3rd cycles (runs 4 and 5, respectively), the 1,3-butadiene conversion passing from 32.8% to a stationary value of about 18%. Elemental analysis proved that the Pd content in the catalyst, after the 3rd cycle, is 20.7% less than that of the original value; however, the above metal decrease is accompanied by a corresponding reduction of the phosphorus content. Therefore, the above findings seem to suggest that the decrease of activity has to be mainly addressed to a superficial erosion of the resin beads by mechanical stirring rather than to a metal leaching into solution. Accordingly no catalytic activity was observed when the products solution, separated from the solid catalyst after the 1st cycle and after addition of fresh 1,3-butadiene to reach the pristine MeOH/C₄H₆ molar ratio, was recycled.

With the aim of improving the catalytic activity of Dow–DPPM–Pd(OAc)₂, the influence of reaction temperature was considered. Indeed, as reported in Table 1, when the temperature was raised from 60° (run 3) to 80°C (run 6), the other parameters held constant, an improvement of 1,3-butadiene conversion from 32.8% to 48.8% was observed. However, a reduction of chemoselectivity to telomers as well as of regioselectivity to the linear ones **1** were also found. The recycles of the solid catalyst (runs 7–10, Table 1) indicate that a progressive decay of the activity occurs, 1,3-butadiene conversion passing from 48.8% to 16.5% from the 1st to the 5th cycle, a deposition of metallic palladium being also observed. Therefore, it may be concluded that the initial improvement of produc-

tivity of the heterogenized catalyst on increasing the reaction temperature is very soon eroded by deactivation phenomena of the catalytic species during the subsequent cycles. In order to improve the performances of the heterogenized catalyst we therefore focused our attention on other reaction parameters and particularly on the use of alkaline alkoxides which not only are known to favour the reduction of Pd(II) to Pd(0) species [12,13] but also may act as nucleophiles in the catalytic cycle [4].

3.2. 1,3-Butadiene telomerization with methanol catalyzed by Dow–DPPM–Pd(OAc)₂ in the presence of sodium methoxide

When 1,3-butadiene telomerization with methanol was carried out in the presence of Dow–DPPM–Pd(OAc)₂ in combination with MeONa as promoter (run 11, Table 2), the other reaction parameters remaining the same as those previously adopted, a much higher activity was observed than that obtained in the absence of the alkoxide activator. Indeed, a quantitative C₄H₆ conversion was obtained against 32.8% (run 3, Table 1). However, a lower overall selectivity to telomers **1** and **2** was found, detectable amounts of trimers and higher telomers being also checked. The recycles of the solid catalyst under the same conditions of run 11, i.e., adding fresh C₄H₆, methanol and MeONa for reaching the relative amounts as those adopted in the 1st cycle, confirmed (runs 12–15) the activation effect of the alkoxide, although a progressive reduction of activity was observed from the 2nd to 5th cycle (Table 2). However, the selectivity of the process remained substantially the same or eventually slightly increased.

With the aim to check if the addition of the alkoxide to the recycled catalyst was really necessary, considering that the activation effect was easily obtained during the 1st catalytic cycle in terms of Pd(II) reduction to Pd(0), a new series of telomerization experiments was performed (Table 3) by using the Dow–DPPM–Pd(OAc)₂ catalyst precursor in the presence of

Table 2

Telomerization of 1,3-butadiene with methanol at 60°C, catalyzed by Dow–DPPM–Pd(OAc)₂ in the presence of MeONa as promoter^a

Run	Reaction time (h)	C ₄ H ₆ conversion (%)	Products (mol%)					R ^b (%)	
			1 ^c	2 ^d	3 ^e	trimers	higher telomers		
11	1st cycle	18	100.0	67.5	9.7	20.1	0.1	2.6	87.4
12	2nd cycle	18	92.0	68.9	8.9	19.5	0.1	2.6	88.5
13	3rd cycle	18	67.6	65.6	11.9	22.1	0.1	0.4	84.7
14	4th cycle	18	65.6	68.1	9.6	22.0	0.1	0.2	87.6
15	5th cycle	18	51.6	70.4	7.7	21.7	0.1	0.1	90.2

^aPd: 0.05 mmol; Pd/P/MeONa/MeOH/C₄H₆ = 1/2/10/3000/2000 mol/mol; *n*-hexane: 20 ml; P_{N₂} = 3 MPa.^bRegioselectivity to the linear telomers **1**, expressed as [1/(1 + 2)] × 100.^c*Cis*- and *trans*-1-methoxy-2,7-octadiene.^d3-Methoxy-1,7-octadiene.^eMainly 1,3,7-octatriene and 4-vinyl-cyclohexene.

MeONa only in the 1st cycle (run 16), no further addition of alkoxide being adopted in the subsequent catalyst recycles (runs 17–20). The decreased activity of Dow–DPPM–Pd(OAc)₂ in run 16 as compared with that of run 11 (Table 2), may be addressed to the lower MeOH/C₄H₆ ratio used (1.36 against 1.5) in the former case. Indeed, the influence on the catalytic activity by the above ratio is more evidenced from the data obtained in runs 22 and 23 (Table 3) where MeOH/C₄H₆ ratios 0.55 and 3.0 were used, respectively. The increase of

the ratio in the above range not only causes an enhancement of activity, the C₄H₆ conversion increasing from 47.9% to 100% but also allows to improve the selectivity to telomers from 63.3% to 87.4% and particularly to reach a 91.7% regioselectivity toward the linear telomers **1**. Analogous results were previously observed [4] in the same reaction catalyzed by the Dow–DPPP–Pd(OAc)₂ catalyst.

When the solid catalyst recovered from run 16 was recycled without addition of fresh MeONa, a reduction of activity was observed until

Table 3

Telomerization of 1,3-butadiene with methanol at 60°C catalyzed by Dow–DPPM–Pd(OAc)₂: effect of the presence of MeONa when added only to the fresh catalyst^a

Run		MeOH/C ₄ H ₆ (mol/mol)	C ₄ H ₆ conversion (%)	Products (mol%) ^b			R ^c (%)
				1 ^d	2 ^e	3 ^f	
16 ^g	1st cycle	1.36	82.3	67.7	9.9	21.7	87.3
17	2nd cycle	1.36	51.0	71.0	12.7	16.2	85.0
18	3rd cycle	1.36	43.7	76.4	14.8	8.8	83.8
19	4th cycle	1.36	46.2	76.3	13.7	9.9	84.8
20	5th cycle	1.36	52.9	73.0	14.8	12.2	83.2
21 ^h	solution recycle	1.36	4.0	59.6	7.7	36.2	88.6
22	1st cycle	0.55	47.9	51.8	11.5	36.1	81.9
23	1st cycle	3.0	100.0	80.1	7.3	12.2	91.7

^aPd: 0.05 mmol; Pd/P/C₄H₆ = 1/2/2200 mol/mol; *n*-hexane: 20 ml; P_{N₂} = 3 MPa; reaction time: 18 h.^bWhen 1 + 2 + 3 < 100, small amounts of trimers and higher telomers are also present.^cSelectivity to the linear telomer **1**, expressed as [1/(1 + 2)] × 100.^d*Cis*- and *trans*-1-methoxy-2,7-octadiene.^e3-Methoxy-1,7-octadiene.^fMainly 1,3,7-octatriene and 4-vinyl-cyclohexene.^gA molar ratio MeONa/Pd = 10 was used.^hThe products solution obtained in run 16, separated from the solid catalyst, was recycled and fresh C₄H₆ added to reach the appropriate MeOH/C₄H₆ ratio.

Table 4

Telomerization of 1,3-butadiene with methanol at 60°C catalyzed by Dow–DPPM–Pd(OAc)₂ in the presence of MeONa and by using a molar ratio MeOH/C₄H₆ = 3^a

Run	C ₄ H ₆ conversion (%)	Products (mol%) ^b			R ^c (%)	
		1 ^d	2 ^e	3 ^f		
24	1st cycle	100.0	80.1	7.3	12.2	91.7
25	2nd cycle	86.0	77.5	12.2	10.1	86.4
26 ^g	solution recycle	8.0	68.1	7.6	24.4	90.0
27	3rd cycle	83.0	77.4	10.7	11.8	87.9
28 ^h	solution recycle	1.6	40.0	5.5	51.9	88.0
29	4th cycle	83.7	78.0	10.7	11.3	88.0

^aPd: 0.05 mmol; Pd/P/C₄H₆ = 1/2/1000 mol/mol; *n*-hexane 20 ml; P_{N₂} = 3 MPa; reaction time: 18 h; MeONa/Pd = 10 mol/mol was used for run 24; no additional MeONa was used for recycle experiments (runs 25–29).

^bWhen 1 + 2 + 3 < 100, small amounts of trimers and higher telomers are also present.

^cRegioselectivity to the linear telomers 1, expressed as [1/(1 + 2)] × 100.

^d*Cis*- and *trans*-1-methoxy-2,7-octadiene.

^e3-Methoxy-1,7-octadiene.

^fMainly 1,3,7-octatriene and 4-vinyl-cyclohexene.

^gThe products solution obtained in run 24, separated from the solid catalyst, was recycled and added with fresh C₄H₆ to reach the MeOH/C₄H₆ ratio equal to 3.

^hThe products solution obtained from run 27 was treated as described in ^g.

a stationary value was reached (about 50% of C₄H₆ conversion), substantially similar to that obtained in the preceding recycle experiments where for each cycle the addition of fresh MeONa was adopted. These results seem to suggest that MeONa behaves as an activator for the catalyst precursor, but when the catalytic species are formed no additional amounts of alkoxide are requested. The recycle (run 21, Table 3) of the products solution deriving from the 1st cycle showed only a very low activity (4% of C₄H₆

conversion), thus suggesting that only traces of Pd are present in the solution.

Recycle experiments of both the solid catalyst (runs 25, 27 and 29, Table 4) and of the products solution (runs 26 and 28) in the telomerization reactions carried out by Dow–DPPM–Pd(OAc)₂, when a MeOH/C₄H₆ molar ratio equal to 3 was adopted, gave substantially the same picture. Indeed, the C₄H₆ conversion reached a stationary value of about 83% after the 2nd recycle, both chemoselectivity to telom-

Table 5

Telomerization of 1,3-butadiene with methanol catalyzed by different heterogenized and homogeneous palladium(II) complexes based on diphosphine chelating ligands, in the presence of MeONa as promoter^a

Run	Catalyst precursor	C ₄ H ₆ /Pd (mol/mol)	C ₄ H ₆ conversion (%)							
			1 h	2 h	3 h	4 h	5 h	6 h	9 h	18 h
30 ^b	Dow–DPPM–Pd(OAc) ₂ ^b	2000	57.6	70.3	83.3	86.5	93.6	96.4	100.0	–
31 ^c	Pd(OAc) ₂ /DPPM ^b	2000	48.9	74.3	88.2	93.3	95.5	100.0	–	–
32	Dow–DPPM–Pd(OAc) ₂ ^c	6500	–	18.0	24.6	–	38.8	53.8 ^d	67.2	100.0
33 ^e	Dow–DPPP–Pd(OAc) ₂ ^c	6500	–	–	13.4	–	–	–	–	97.0

^aReaction conditions: T = 60°C; P_{N₂} = 3 MPa; MeONa/Pd, P/Pd and MeOH/C₄H₆ = 10, 2 and 1.5 mol/mol, in that order.

^bPd = 0.05 mmol; *n*-hexane: 20 ml.

^cPd = 0.08 mmol; in the absence of *n*-hexane.

^dAfter 7 h.

^eRef. [4].

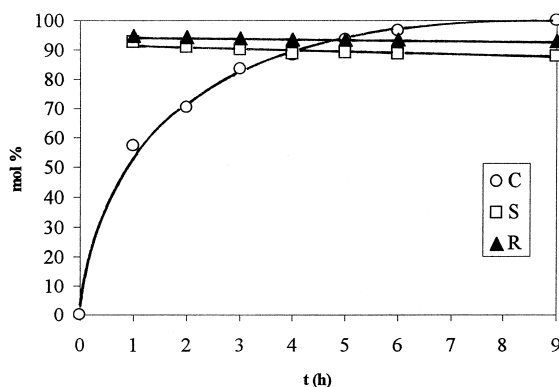


Fig. 1. Time evolution of C_4H_6 conversion (C), chemoselectivity (S) and regioselectivity (R) to telomers in the 1,3-butadiene telomerization with methanol catalyzed by the Dow-DPPM-Pd(OAc)₂/MeONa system in the presence of *n*-hexane (run 30).

ers and regioselectivity to the linear telomers **1** reaching a steady value around 88%, thus substantiating further the really heterogeneous character of the above supported catalyst.

In order to get a better insight about the time evolution of the C_4H_6 conversion as well as of the distribution of the reaction products, the telomerization reaction catalyzed by the Dow-DPPM-Pd(OAc)₂/MeONa system (run 30) was studied and the results were reported in Table 5 and in Fig. 1. The above data indicate that after 1 h almost 60% of 1,3-butadiene was reacted, the conversion was completed after 9 h of reaction. The profile of the C_4H_6 conversion as a function of reaction time (Fig. 1) clearly shows

that the induction period of the reaction is very short if any, due to the fast activation effect of MeONa.

Finally, as far as the chemoselectivity (S) to telomers and the regioselectivity (R) to the linear telomers **1** are concerned, we may conclude that the former decreases from 92.8% to 87.8% and the latter from 94.9% to 93.3% in the 1- to 9-h range (Fig. 1), thus both values remaining appreciably high during the overall course of the reaction.

A comparison of Dow-DPPM-Pd(OAc)₂ with the homogeneous system Pd(OAc)₂/DPPM (P/Pd = 2) under the same experimental conditions (runs 30 and 31, Table 5) allows to observe that the former, in the presence of MeONa as promoter, displays a slight lower overall activity than the latter. In fact, whereas the heterogenized system displays a higher C_4H_6 conversion after 1 h of reaction (57.4% against 48.9%), subsequently the homogeneous system prevails affording a 100% C_4H_6 conversion after 6 h against 96.4% of the counterpart, the above findings substantially indicating that the two systems have similar activity. Indeed, Dow-DPPM-Pd(OAc)₂ and Pd(OAc)₂/DPPM show after 6 h 199 and 217 turnover numbers (T.N.) values, respectively, as reported in Table 6. Finally, as far as the selectivity of the process is concerned, good performances were obtained for the heterogenized system, although slightly

Table 6

Productivity and selectivity in 1,3-butadiene telomerization with methanol catalyzed by the heterogenized Dow-DPPM-Pd(OAc)₂ system as compared with the corresponding homogeneous analog, in the presence of MeONa as promoter^a

Run	Catalyst precursor	Products (mol%) ^{b,c}			<i>R</i> ^{b,d} (%)	T.N. ^{b,e}
		1 ^f	2 ^g	3 ^h		
30	Dow-DPPM-Pd(OAc) ₂	82.9	6.0	10.8	93.3	199
31	Pd(OAc) ₂ /DPPM	89.6	5.6	4.7	94.1	217

^a Reaction conditions: Pd: 0.05 mmol; Pd/P/MeONa/MeOH/ C_4H_6 = 1/2/10/3000/2000 mol/mol; *n*-hexane: 20 ml; P_{N_2} = 3 MPa.

^b Values referred to 6 h reaction time.

^c When **1** + **2** + **3** < 100, small amounts of trimers and higher telomers are also present.

^d Regioselectivity to the linear telomers **1**, expressed as $[1/(1+2)] \times 100$.

^e Turnover number (T.N.) expressed as: g (products)/g (Pd) × h.

^f *Cis*- and *trans*-1-methoxy-2,7-octadiene.

^g 3-Methoxy-1,7-octadiene.

^h Mainly 1,3,7-octatriene and 4-vinyl-cyclohexene.

Table 7

Telomerization of 1,3-butadiene with methanol catalyzed by the Pd(OAc)₂/DPPM homogeneous system: influence of the MeONa promoter on catalyst productivity and selectivity^a

Run	2 (MeONa/Pd = 0)				31 (MeONa/Pd = 10)					
	1 h	2 h	3 h	4 h	1 h	2 h	3 h	4 h	5 h	6 h
C ₄ H ₆ conversion (%)	33.5	50.6	69.6	96.0	48.9	76.3	88.2	93.3	95.5	100.0
S (%) ^b	95.5	95.3	95.2	95.1	95.7	95.7	95.7	95.6	95.3	95.2
R (%) ^c	93.8	93.8	93.3	93.2	96.7	96.8	95.1	95.1	94.2	94.1

^aReaction conditions: Pd = 0.05 mmol; Pd/P/MeOH/C₄H₆ = 1/2/3000/2000 mol/mol; solvent (*n*-hexane): 20 ml; *T* = 60°C; *P*_{N₂} = 3 MPa.

^bChemoselectivity to telomers.

^cRegioselectivity to linear telomers **1**, expressed as $[1/(1 + 2)] \times 100$.

inferior to those of the homogeneous analog, particularly in terms of chemoselectivity to telomers (Table 6).

It is worth noting that the addition of MeONa as promoter to the Pd(OAc)₂/DPPM homogeneous system causes an increase of the reaction rate, an improvement of C₄H₆ conversion being observed at equal reaction time when MeONa is present (Table 7). This indicates that even in homogeneous phase MeONa accelerates the reduction of Pd(II) to Pd(0) species; moreover, the selectivity to telomers is not substantially affected by the presence of MeONa, although a better regioselectivity is observed.

In order to compare the activity of Dow–DPPM–Pd(OAc)₂ with the corresponding heterogenized system Dow–DPPP–Pd(OAc)₂ based on DPPP chelating moieties previously reported [4], a telomerization experiment was performed (run 32, Table 5), in the presence of MeONa as promoter under the same experimental conditions previously adopted for Dow–DPPP–Pd(OAc)₂ (run 33, Table 5). From the data of C₄H₆ conversion after 3 h (24.6% and 13.4% for runs 32 and 33, respectively) it may be concluded that Dow–DPPM–Pd(OAc)₂ system displays a significantly higher activity than the Dow–DPPP–Pd(OAc)₂ system. Moreover, from the plot of the C₄H₆ conversion (*C*) as a function of reaction time (Fig. 2), it is possible to evaluate that the completeness of the reaction for the Dow–DPPM–Pd(OAc)₂ system is afforded at a significantly shorter time than 18 h,

as indicated in Table 5, thus confirming the above statement (for the Dow–DPPP–Pd(OAc)₂ system the C₄H₆ conversion was not complete after 18 h). Moreover, from the plot of chemoselectivity (*S*) to telomers and regioselectivity (*R*) to the linear telomers **1**, as reported for the Dow–DPPP–Pd(OAc)₂ system in Fig. 2, values of 93.4% and 92.2% after 3 h, respectively, were obtained against the corresponding values of 76.1% and 94.6% for Dow–DPPP–Pd(OAc)₂ [4], thus allowing to appreciably improve the percentage of the linear telomers in the reaction mixture. Therefore it may be concluded that the heterogenization of Pd(II) species on the polymeric support through bis(diphenylphosphino) methane moieties affords a catalyst precursor with improved performances in terms of both

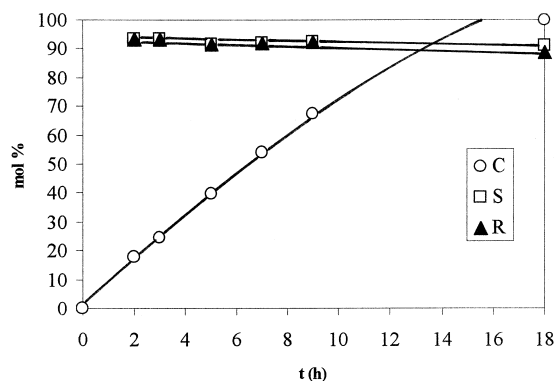


Fig. 2. Time evolution of C₄H₆ conversion (*C*), chemoselectivity (*S*) and regioselectivity (*R*) to telomers in the 1,3-butadiene telomerization with methanol catalyzed by the Dow–DPPM–Pd(OAc)₂/MeONa in the absence of *n*-hexane (run 32).

activity and selectivity than that obtained via the DPPP ligand. The above findings allow to confirm that diphosphine ligands, such as DPPP, affording more stable six-membered metallacyclo moieties, undergo palladium complexes characterized by a lower catalytic activity in the 1,3-butadiene telomerization with methanol.

3.3. Telomerization of 1,3-butadiene with methanol catalyzed by Pst-DPPM-Pd(OAc)₂ in the presence of MeONa as promoter: influence of the reaction medium

As previously reported [8], poly(styrene), when functionalized to a low extent with DPPM moieties (Pst-DPPM), is soluble in most organic solvents, particularly in aromatic hydrocarbons and ether compounds. However, it is worth noting that Pst-DPPM, when reacted with Pd(OAc)₂, gives rise to the insoluble Pst-DPPM-Pd(OAc)₂ complex [8]. Moreover, when this is used as catalyst for the 1,3-butadiene telomerization with methanol, the alcohol, which is a non solvent for poly(styrene) and its derivatives, favours the heterogeneity of the catalytic system. However, the contemporary use of an organic diluent in the reaction mixture may differently affect the swelling of the polymeric ligand, depending on its solvation properties. Therefore, taking into account that the catalyst prepared from the linear poly(styrene), due to the enhanced mobility of the macromolecules with respect to the corresponding system obtained from the crosslinked Dow-B resin, would be more sensitive to solvation effects, the influence of reaction medium on the catalytic activity of the Pst-DPPM-Pd(OAc)₂/MeONa heterogeneous system was studied.

As reported in Table 8, telomerization experiments (runs 34–37) were performed at 60°C under the same experimental conditions except for the presence of different solvents. The results clearly indicate that when hydrocarbon solvents, such as toluene (run 35) and *n*-hexane (run 37), were used a much higher activity was observed with respect to that found when ether

Table 8

Telomerization of 1,3-butadiene with methanol catalyzed by Pst-DPPM-Pd(OAc)₂ in the presence of MeONa as promoter: influence of solvent nature^a

Run	Solvent	C ₄ H ₆ conversion (%)	Products (mol%) ^b			R ^c (%)
			1 ^d	2 ^e	3 ^f	
34	Dioxane	22.6	22.4	2.6	74.6	89.5
35	Toluene	72.2	59.1	7.7	32.2	88.5
36	THF	11.3	28.7	2.7	67.7	91.3
37	<i>n</i> -hexane	74.0	71.4	10.0	18.1	87.7

^aPd = 0.05 mmol; Pd/P/MeONa/MeOH/C₄H₆ = 1/2/10/3000/3000 mol/mol; T = 60°C; solvent: 20 ml; reaction time: 18 h; P_{N₂} = 3 MPa.

^bWhen 1+2+3 < 100, small amounts of trimers and higher telomers are also present.

^cRegioselectivity to the linear telomers 1, expressed as [1/(1+2)] × 100.

^dCis- and trans-1-methoxy-2,7-octadiene.

^e3-Methoxy-1,7-octadiene.

^fMainly 1,3,7-octatriene and 4-vinyl-cyclohexene.

solvents, i.e., THF (run 36) and dioxane (run 34), were employed. Indeed C₄H₆ conversions in the 72–74% range were found with the former solvents, whereas only 11–23% conversions were obtained with the latter solvents. Taking into account that toluene and THF are good solvents for poly(styrene) and better than dioxane and *n*-hexane, in that order, the above results seem to suggest that no correlation exists between polymer swelling extent and activity of the catalyst. This implies that the catalytic process is not diffusion controlled, the active sites being mainly located on the surface of the polymeric support. Therefore the dramatic reduction of activity caused by the presence of ethers has to be related to their electron donor character [14], THF and dioxane competing with the reagents in the coordination to the palladium species through their oxygen electron pairs. Moreover, in the presence of ethers, a drop of chemoselectivity to telomers was found (Table 8), the production of dimers being higher than 67%. This can be tentatively explained by assuming that the coordination of the solvent increases both the steric hindrance and the electronic density around the metal, thus preventing the nucleophilic methanol attack and hence

favouring the elimination reaction to dimeric products. Indeed, analogous results were previously observed also in the 1,3-butadiene telomerization with methanol catalyzed by Pst–DPPP–Pd(OAc)₂ [4].

4. Conclusions

On the basis of the obtained results the following concluding remarks can be drawn.

(i) Heterogenized palladium(II) complexes on polymeric supports through bis(diphenylphosphino) methane moieties, such as Dow–DPPM–Pd(OAc)₂, display, even in the absence of alkoxide promoters, an appreciable catalytic activity in the telomerization of 1,3-butadiene with methanol and result more active as compared with analogous systems supported via DPPP chelating ligands. Moreover, under proper reaction conditions, the above system does not release any appreciable amount of metal species into the solution after several recycles, thus working as a real heterogeneous catalyst.

(ii) Dow–DPPM–Pd(OAc)₂, when activated by an alkoxide promoter, reaches a high catalytic activity, the chemoselectivity to telomers and the regioselectivity to linear telomers being only slightly lower as compared with the corresponding homogeneous system. The above supported system behaves substantially as a heterogeneous catalyst also in the presence of the alkoxide promoter which, however, is not required to be added any further in the subsequent recycles. Moreover, the results obtained allow to conclude that diphosphine ligands, such as DPPM, affording less stable four-membered metallacyclo moieties, give rise to palladium complexes characterized, also in the presence of an alkaline alkoxide, by a higher catalytic activity in the 1,3-butadiene telomerization with methanol.

(iii) The catalytic activity of the above heterogenized complexes, as evidenced by telomerization experiments carried out with the PSt–DPPM–Pd(OAc)₂/MeONa system, does not

seem to be appreciably affected by the degree of swelling of the polymeric support and hence by diffusion properties of the catalyst, the metal sites probably being mainly located on the surface of the polymeric support. The data obtained suggest also that ether solvents must be avoided because they compete with 1,3-butadiene in the coordination to the metal, thus strongly reducing both the activity and the chemoselectivity to telomers.

(iv) The real heterogeneous character of the above supported catalytic systems, as ascertained under so severe conditions as those involved in the 1,3-butadiene telomerization reaction, likely makes them suitable to be used as heterogenized systems also in several other palladium catalyzed reactions.

References

- [1] C.U. Pittman, Jr., in: G. Wilkinson, F.G.A. Stone (Eds.), *Comprehensive Organometallic Chemistry*, Vol. 8, Pergamon, Oxford, 1982, p. 553.
- [2] A.D. Pomogailo, *Russian Chem. Rev.* 61 (1992) 133.
- [3] H. Hirai, N. Toshima, in: Y. Iwasawa (Ed.), *Tailored Metal Catalysts*, Reidel, Dordrecht, 1986, p. 87.
- [4] F. Benvenuti, C. Carlini, A.M. Raspolli Galletti, G. Sbrana, M. Marchionna, R. Patrini, *J. Mol. Catal. A: Chem.* 137 (1999) 49.
- [5] M. Marchionna, R. Patrini, F. Giavazzi, G.C. Pecci, Preprints 212th National Meeting of the American Chemical Society, 1996, Div. Petr. Chem., Vol. 41, p. 585.
- [6] A. Behr, in: R. Ugo (Ed.), *Aspects of Homogeneous Catalysis*, Vol. 5, Reidel, Dordrecht, 1984, p. 3.
- [7] F. Benvenuti, C. Carlini, M. Marchionna, R. Patrini, R. Pieri, A.M. Raspolli Galletti, G. Sbrana, Proc. of the XII National Congress of Industrial Chemistry and Catalysis Symposium of Ital. Chem. Soc., Giardini Naxos (CT), Italy, 22–25 June 1997, p. 107 (manuscript submitted to *J. Mol. Catal. A: Chem.*).
- [8] F. Benvenuti, C. Carlini, M. Marchionna, R. Patrini, A.M. Raspolli Galletti, G. Sbrana, *J. Inorg. Organometal. Polym.* 7 (1997) 183.
- [9] M.F. Rettig, P.M. Maitlis, *Inorg. Synth.* 28 (1990) 110.
- [10] S. Fisher, J. Porter, *Anal. Chem.* 36 (1964) 1159.
- [11] R. Patrini, M. Lami, M. Marchionna, F. Benvenuti, A.M. Raspolli Galletti, G. Sbrana, *J. Mol. Catal. A: Chem.* 129 (1998) 179.
- [12] D. Commereuc, Y. Chauvin, *Bull. Chim. Soc. Fr.* (1974) 656.
- [13] W. Kuran, A. Musco, *Inorg. Chim. Acta* 12 (1975) 187.
- [14] V. Gutmann, *Coord. Chem. Rev.* 18 (1976) 225.