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Highly Efficient Catalytic System for the CO/Styrene Copolymerization: Toward the Stabilization of the Active Species

Barbara Milani,* Gianni Corso, and Giovanni Mestroni

Dipartimento di Scienze Chimiche, Università di Trieste, Via Licio Giorgieri 1,
34127 Trieste, Italy

Carla Carfagna and Mauro Formica

Istituto di Scienze Chimiche, Università di Urbino, P.zza Risorgimento 6, 61029 Urbino, Italy

Roberta Seraglia

CNR, Area di Ricerca di Padova, Corso Stati Uniti 4, 35020 Padova, Italy

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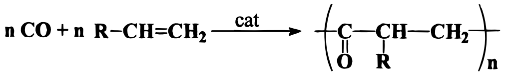
The CO/styrene copolymerization reaction promoted by $[Pd(N{-}N)_2][PF_6]_2$ (N−N = 2,2′-bipyridine (bpy), 1,10-phenanthroline (phen)) complexes was investigated in detail. The stability of the catalytic system is mainly influenced by the nature of the reaction medium. By virtue of the high stability of the active species in 2,2,2-trifluoroethanol compared to methanol, no addition of 1,4-benzoquinone is required for the reaction. The analysis of the parameters that affect the stability of the catalyst when no oxidant is added revealed that (i) phen is a better ligand than bipy and the catalyst generated by the complex $[Pd(phen)_2][PF_6]_2$ is active at least up to 48 h of reaction, yielding a productivity as high as 5.4 kg CP/g Pd; (ii) the stability is enhanced by addition of a mixture of the N−N ligand and the corresponding monoprotonated salt $[(N{-}N)H][PF_6]$; (iii) a relatively high carbon monoxide pressure is required to protect the catalyst toward its decomposition. A correlation between these parameters and the molecular weight of polyketones produced was also found. In trifluoroethanol, with no benzoquinone added, CO/styrene polyketones with M_w values as high as 80 000 were synthesized for the first time. The copolymers were analyzed by MALDI-TOF spectrometry to characterize their end groups. One of the end groups of the polyketones prepared in trifluoroethanol is always the unsaturated ketone, while the other one is either the saturated ketone or the carboalcohoxy moiety. The mechanistic implications deriving from this analysis are discussed.

Introduction

The carbon monoxide−olefin co- and terpolymerization reactions (eq 1) represent a very attractive field of research, thanks to the ready availability of base materials and, above all, to the unique combination of performance properties shown by the products.[1−5] These polymers have a polyketone structure with a perfect alternation of the two monomeric units along the main chain. The CO/ethylene/propylene terpolymer is now commercialized by the Shell Chemical Company with the name of Carilon.[6]

From a general point of view, the catalytic systems applied to the CO/olefin copolymerization reactions are formed by a palladium(II) salt modified by a bidentate phosphorus- or nitrogen-donor chelating ligand. The reactions are usually performed in methanol; different cocatalysts (e.g., Brønsted acids) and/or co-reagents (e.g., oxidants) may be required, depending if in situ catalytic systems or preformed complexes are being used.[2] In



$$n\,CO + n\ R{-}CH{=}CH_2 \xrightarrow{cat} \left(\underset{\overset{\|}{O}}{C} - \underset{\overset{|}{R}}{CH} - CH_2 \right)_n \qquad (1)$$

R = H, CH_3, Ph

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* Corresponding author. Fax: +39 040 6763903. E-mail: milani@dsch.univ.trieste.it.

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particular, for the CO/styrene copolymerization, nitrogen-donor chelating ligands are necessary,[7] even though a catalytic system based on a phosphino-phosphito ligand has been recently reported to promote this copolymerization.[8]

Brookhart et al. demonstrated that the stereochemistry of the polymer can be properly controlled: their catalytic system produced syndiotactic or isotactic or stereoblock polyketones, depending on the nature of the N−N ligand used.[9,10] Very recently Consiglio et al. demonstrated that also the regiochemistry of the polyketone can be strictly controlled: the use of N−N ligands led to regioregular copolymers (originated by an exclusively secondary insertion of styrene), while P−N ligands led to regioirregular products.[11]

Nevertheless, the CO/styrene polyketone has never been obtained both in high yield and with a molecular weight as high as required for industrial applications.[12] One of the main reasons for this is the instability of the active species, which decomposes to palladium metal during the reaction.

For several years we have been involved in the synthesis and characterization of dicationic bischelated Pd(II) compounds of general formula $[Pd(N-N)_2][X]_2$ (N−N = 2,2′-bipyridine (bpy), 1,10-phenanthroline (phen) and their substituted derivatives; X = PF_6^-, BF_4^-, OTs, OTf). Recently, we found that $[Pd(bpy)_2][PF_6]_2$ promotes CO/styrene copolymerization in 2,2,2-trifluoroethanol (TFE), yielding the copolymer in high yield, without apparent decomposition to palladium metal. In this solvent, unlike in methanol, the catalytic species are still completely active after 48 h of reaction and yield a white copolymer with a productivity of 17 kg CP/g Pd (kg CP/g Pd = kilograms of copolymer per gram of palladium).[13] Moreover, the achievement of such high productivity did not require a large excess of oxidant.

Table 1. CO/Styrene Copolymerization: Effect of Solvent, of Benzoquinone, and of Nitrogen-Donor Ligand. Catalyst Precursor: $[Pd(N-N)_2][PF_6]_2$[a]

run	N−N	solvent	[BQ]/[Pd]	g CP	kg CP/g Pd	$\langle M_w \rangle$ ($\langle M_w \rangle / \langle M_w \rangle$)
1	bpy	MeOH	64	0.97	1.7	10 000 (1.4)
2	bpy	MeOH		0.11	0.2	16 000 (1.6)
3	bpy	TFE	64	2.33	4.1	58 500 (2.3)
4	bpy	TFE		1.03	1.8	85 000 (1.8)
5	phen	TFE	64	1.27	2.2	66 000 (1.9)
6	phen	TFE		1.02	1.8	72 000 (1.8)

[a] Reaction conditions: $n_{Pd} = 0.54 \times 10^{-2}$ mmol; styrene $V = 30$ mL; solvent $V = 20$ mL; DMP $V = 0.5$ mL; $T = 60$ °C; $P_{CO} = 40$ atm; $t = 14$ h.

In this paper we present a detailed investigation of the catalytic system reported above in the absence of 1,4-benzoquinone. In particular, the effect of the parameters that influence the stability of the active species will be presented. Moreover, the analysis of the polyketones through matrix-assisted laser desorption/ionization (MALDI) mass spectrometry[14] allowed us to characterize their end groups and, therefore, to speculate on the processes involved in the initiation and termination steps of the copolymerization catalytic cycle.

Results

CO/Styrene Copolymerization. The CO/styrene copolymerization reactions were carried out in trifluoroethanol and, for comparative purposes, in methanol, with $[Pd(N-N)_2][PF_6]_2$ complexes as catalyst precursors and with 2,2-dimethoxy propane (DMP) as drying agent, to minimize the presence of water in the reaction mixture. (The presence of water may favor the decomposition of catalyst to metal.)

In the literature the oxidant, usually 1,4-benzoquinone, is claimed as an essential component of the catalytic systems based on N-donor ligands, operating in methanol.[2] The high stability of the catalyst in trifluoroethanol with respect to methanol prompted us to investigate the effect of benzoquinone on the productivity and the molecular weight of polymeric materials. While in the presence of the oxidant ([BQ]/[Pd] = 64) the productivity of $[Pd(bpy)_2][PF_6]_2$ in trifluoroethanol is twice that in methanol (Table 1, runs 1, 3), it becomes 9 times higher without benzoquinone (Table 1, runs 2, 4). In agreement with the literature,[7a] in both solvents, the molecular weight of the copolymer increases when the reactions are performed without the oxidant (Table 1, runs 1−4). In all cases polyketones prepared in trifluoroethanol have a molecular weight 5 times higher than those prepared in methanol (Table 1, runs 1−4). Therefore, operating in trifluoroethanol, without ben-

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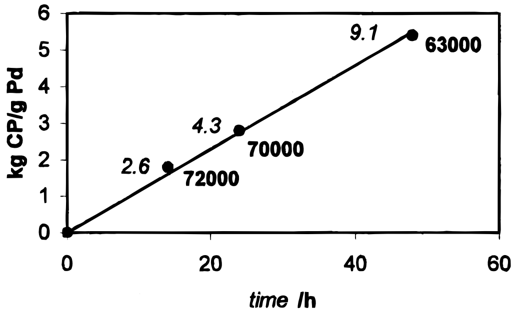

Figure 1. CO/styrene copolymerization: effect of time. Catalyst precursor: $[Pd(phen)_2][PF_6]_2$. Reaction conditions: see Table 1; solvent TFE $V = 20$ mL. The values reported near the points are $\langle M_w \rangle$ in bold; number of cycles calculated as mol CP/mol Pd in italics.

zoquinone, CO/styrene polyketones with a molecular weight of 85 000 are easily obtained (Table 1, run 4).

The results reported in Table 1 indicate that, unlike in methanol, in trifluoroethanol benzoquinone is not required to promote the reaction, even if the productivity is higher when the oxidant is present. Moreover, the high values of molecular weight obtained in the fluorinated alcohol indicate that the ratio between the propagation rate and the termination one is higher in this solvent compared to methanol.

Although the catalyst is still active without the oxidant, a partial decomposition of the active species to metal occurs (gray copolymer). As first step toward its stabilization, the nature of the nitrogen ligand was investigated. While $[Pd(bpy)_2][PF_6]_2$, in the presence of oxidant, shows an activity that is almost twice that of $[Pd(phen)_2][PF_6]_2$, their productivities become comparable when no benzoquinone is used (Table 1, runs 3−6). Under these conditions, however, the copolymer obtained with the phen ligand is white, suggesting a very limited decomposition to Pd metal. Indeed, an approximately linear relationship between productivity and time is found with the complex $[Pd(phen)_2][PF_6]_2$ (Figure 1). The catalyst is active at least up to 48 h of reaction, yielding a productivity as high as 5.4 kg CP/g Pd. The molecular weight of the copolymer is only slightly affected by the reaction time (Figure 1), thus indicating that the increase of productivity is due to an increase of the number of cycles rather than to a variation of the ratio between the propagation and the termination rate.

The productivity is also influenced by the pressure of carbon monoxide, but the effect is different if the oxidant is present or not (Table 2). As already observed by Brookhart[4m] and by us,[13,15] when the copolymerization is carried out with an excess of benzoquinone with respect to palladium, the inhibiting effect of CO is evident. On the contrary, when no oxidant is present, the productivity of the catalytic system decreases slightly on lowering the CO pressure (Table 2). This behavior may be related to the progressive loss of stability of the catalyst, as evidenced also by formation of palladium metal at the end of the run when an initial CO pressure of 10 atm was used. The inhibiting role of CO becomes relevant only at relatively high pressure (50 atm). Moreover, on decreasing the initial CO pressure, polyketones of low molecular weight are obtained (Table 2). Therefore, when no oxidant is present, a proper pressure of carbon monoxide is important both to ensure the stability of the active species and to obtain CO/styrene polyketones of high molecular weight.

Table 2. CO/Styrene Copolymerization: Effect of CO Pressure. Catalyst Precursor: $[Pd(phen)_2][PF_6]_2$[a]

P_{CO} (atm)	[BQ]/[Pd]	kg CP/g Pd	$\langle M_w \rangle$ ($\langle M_w \rangle / \langle M_n \rangle$)
40	64	3.9	n.d.
20	64	7.1	n.d.
10	64	9.9	n.d.
50	0	2.3	80 000 (1.9)
40	0	2.8	70 000 (2.2)
20	0	2.6	53 500 (2.3)
10	0	2.0	36 000 (2.0)

[a] Reaction conditions: see Table 1; solvent TFE $V = 20$ mL; $t = 24$ h.

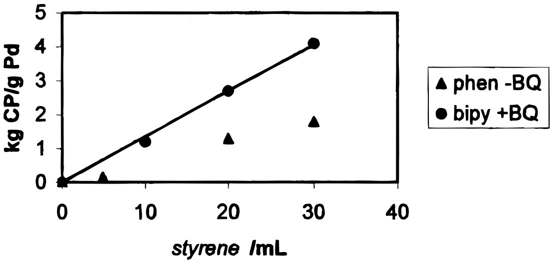

Figure 2. CO/styrene copolymerization: effect of the amount of olefin. Catalyst precursor: $[Pd(N-N)_2][PF_6]_2$. Reaction conditions: $n_{Pd} = 0.54 \times 10^{-2}$ mmol; solvent TFE $V = (50 - V_{styr})$ mL; DMP $V = 0.5$ mL; $P_{CO} = 40$ atm; $T = 60$ °C; $t = 14$ h; with N−N = phen [BQ]/[Pd] = 0; with N−N = bipy [BQ]/[Pd] = 64.

Table 3. CO/Styrene Copolymerization: Effect of Cocatalyst. Catalyst Precursor: $[Pd(phen)_2][PF_6]_2$[a]

[(phen)H]/[Pd][b]	[phen]/[Pd][c]	kg CP/g Pd	$\langle M_w \rangle$ ($\langle M_w \rangle / \langle M_n \rangle$)	N.C.[d]
0	0	2.0	36 000 (2.0)	6
1.0	0.5	3.1	36 000 (2.0)	9
1.5	0.5	5.3	32 000 (2.0)	18
2.0	0.5	4.6	33 000 (1.9)	15

[a] Reaction conditions: see Table 1; solvent TFE $V = 20$ mL; $P_{CO} = 10$ atm; $t = 24$ h. [b] (phen)H was added as $[(phen)H][PF_6]$ salt. [c] phen added at the reaction mixture. [d] N.C. = Number of cycles calculated as mol CP/mol Pd.

The concentration of the olefin comonomer is also important for the stability of the catalyst. In the presence of the oxidant we found an approximately linear relationship between the productivity and the initial amount of styrene (Figure 2). Without the oxidant a poor catalytic activity, accompanied by a significant decomposition to Pd metal, was observed with the lowest amount of olefin (5 mL). A 4-fold increase of the amount of olefin induced an increase of prouctivity of almost 1 order of magnitude.

The effect of the addition of mixtures of phen and different amounts of $[(phen)H][PF_6]$ was investigated at 10 atm of CO (Table 3). In all cases an increase of productivity was found with respect to $[Pd(phen)_2][PF_6]_2$, while no variation of the molecular weight was observed. Therefore, the slight excess of nitrogen ligand together with the weak acid $[(N-N)H]^+$ significantly increases the stability of the active species, as evidenced by the increase of the number of cycles from 6 up to 18

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Table 4. CO/Styrene Copolymerization: Effect of DMP. Catalyst Precursor: $[Pd(phen)_2][PF_6]_2$[a]

DMP (mL)	P_{CO}(atm)	kg CP/g Pd	$\langle M_w \rangle$ ($\langle M_w \rangle / \langle M_n \rangle$)
0.5	40	2.8	70 000 (2.2)
0	40	2.9	89 000 (2.0)
0.5	10	2.0	36 000 (2.0)
0	10	2.0	40 000 (2.0)

[a] Reaction conditions: see Table 1; solvent TFE $V = 20$ mL; $t = 24$ h.

(Table 3). These two cocataysts have no effect on the ratio between the propagation and the termination rate.

Even though all the experiments were carried out in the presence of dimethoxypropane, we found that this drying agent is unnecessary for the reaction. No variation in the productivity was found when the copolymerization was carried out without DMP, both at 40 and 10 atm (Table 4); rather, a slight increase of molecular weight was observed, suggesting that traces of water have no negative effect on the catalytic system.

MALDI Analysis. Some of the polyketones prepared with this catalytic system were analyzed by MALDI/MS. MALDI can produce intact molecular ions with molecular masses up to 10^6 Da. The sample solution is generally mixed with a light-absorbing matrix solution, leading to a sample-to-matrix ratio of 1:10 000 for protein or 1:1000 (or less) for synthetic polymers. The resulting mixture is deposited and dried on a laser target surface. The incidental laser energy is absorbed by the matrix, leading, through the formation of a "plume", to the desorption of intact molecular ions of the analyte, generally single charged, in the gas phase. MALDI/MS technique has been successfully applied in the polymer analysis for the determination of both molecular weight distribution and end groups.

The MALDI mass spectra of some of the polyketones are reported in Figures 3, 4, and 5.

The MALDI/MS data on the molecular weight distribution are different from those obtained by GPC analysis. This can be explained by considering that MALDI/MS can give results in good agreement with molecular weight distribution data from traditional measurements only when the polymers have low polydispersity ($M_w/M_n < 1.4$).[16] For higher polydispersity, the values obtained by MALDI/MS are underestimated. Moreover, the detector saturation due to the continuous stream of low molecular weight species causes a loss of sensitivity at high molecular masses.[17] However, MALDI/MS can be used to determine end groups from their mass, which can be calculated by subtracting the appropriate number of monomer units (and the mass of the cation) from the mass of a given molecular ion. In particular the recent development of MALDI time-of-flight (TOF) instruments with high mass resolution allows us to obtain isotope distributions for each ionic species, leading to a more accurate determination of the end groups.[18]

The MALDI mass spectra of all the polymers examined are characterized by the presence of cationized (adducts with sodium and potassium) oligomers that differ from each other by the mass of the repeat unit.

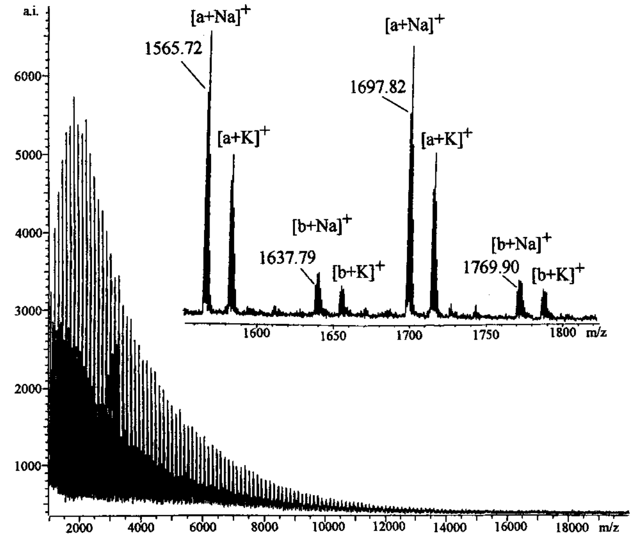
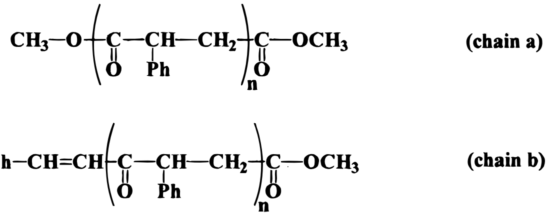


Figure 3. MALDI-TOF mass spectrum of a CO/styrene copolymer prepared in methanol: (a) full spectrum; (b) an enlarged region.

Scheme 1. Polymeric Chains Present in a CO/Styrene Polyketone Prepared in Methanol



In Figure 3 the MALDI mass spectrum of a CO/styrene copolymer prepared in methanol (Table 1, run 1) is shown. Two different polymeric chains (a and b), differing only in the end groups, are present. One polymer has two carbomethoxy end groups (Scheme 1: chain a), while the other has one carbomethoxy and one unsaturated end group (Scheme 1: chain b); only the most likely of the two possible unsaturated end groups is indicated. In agreement with the literature, no saturated end groups are observed.[7a]

The MALDI mass spectrum of a polyketone prepared in trifluoroethanol, without benzoquinone (Table 2, run 7), evidences the presence of three different polymeric chains (Figure 4). All of them have in common one unsaturated end group, while the other one is different in each case. One chain terminates with a saturated group, and two different alkyl groups are possible (Scheme 2: chains a and a′). The other two polymeric chains terminate with an ester end group, which derives either from methanol (Scheme 2: chain b) or from trifluoroethanol (Scheme 2: chain c), respectively. Methanol is originated by the reaction of dimethoxypropane with water.

In agreement with this interpretation, the MALDI spectrum of a CO/styrene polyketone prepared in tri-

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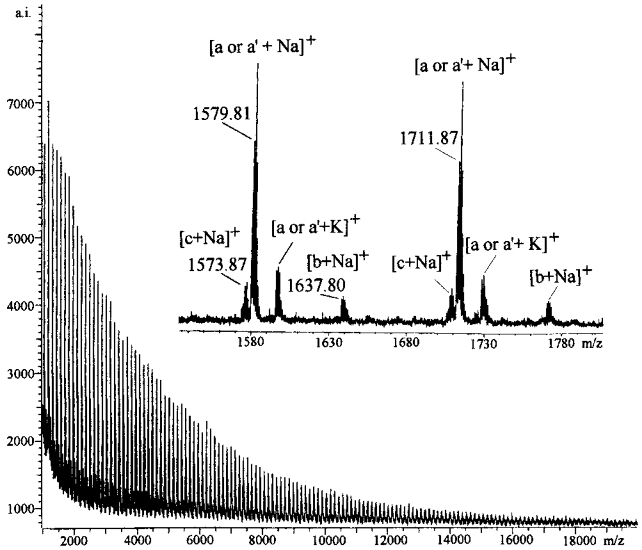
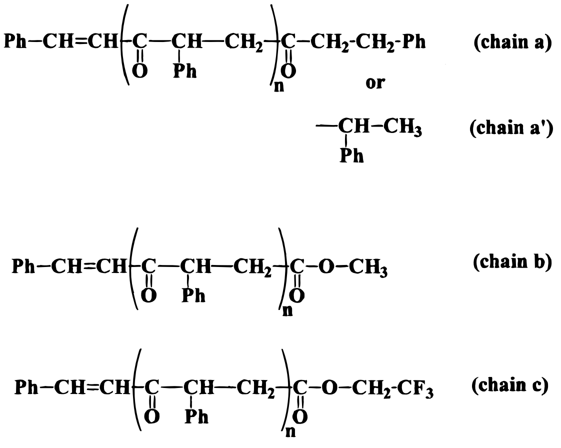


Figure 4. MALDI-TOF mass spectrum of a CO/styrene copolymer prepared in trifluoroethanol without BQ: (a) full spectrum; (b) an enlarged region.

Scheme 2. Polymeric Chains Present in a CO/ Styrene Polyketone Prepared in Trifluoroethanol



fluoroethanol, without both benzoquinone and dimethoxypropane (Table 4, run 4), evidences only the two polymeric chains a/a′ and c and shows no trace of chain b with the carbomethoxy end group (Figure 5).

Discussion

Several papers have dealt with the mechanism of the carbon monoxide/olefin copolymerization reaction.[4d,h,p,19] It is generally accepted that the catalytic cycle can be divided in three parts: the initiation, the propagation, and the termination steps. The alternating insertion of CO into the palladium−alkyl bond followed by that of the alkene into the palladium−acyl bond was unequivocally demonstrated, for the first time, by Vrieze and Elsevier.[20] These stepwise reactions constitute the propagation step, which is recognized to be the same in all of the copolymerization processes, while the initiation and termination steps depend on the nature of both the olefin comonomer and the catalytic system.

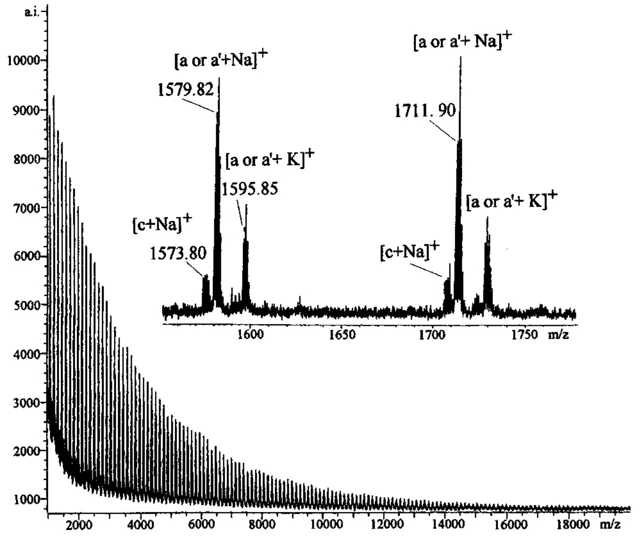
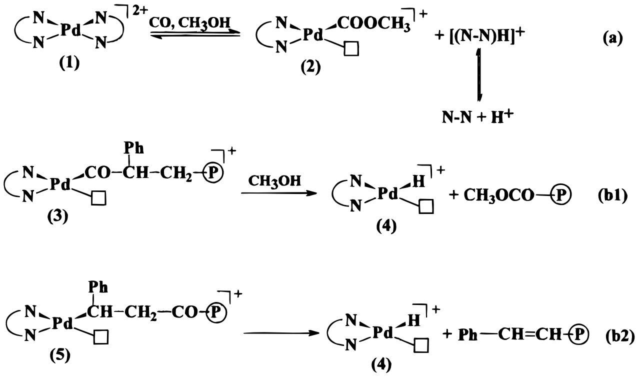


Figure 5. MALDI-TOF mass spectrum of a CO/styrene copolymer prepared in trifluoroethanol without BQ and without DMP: (a) full spectrum; (b) an enlarged region.

Scheme 3. Reaction Mechanism in Methanol[a]



[a] (a) Initiation step: carbomethoxy pathway. (b) Termination steps: (1) methanolysis, (2) β-hydrogen elimination.

The MALDI analysis evidenced that the nature of the end groups strongly depends on the reaction medium. Therefore, for this catalytic system different mechanisms are operative in the two solvents.

According to Drent,[2] in methanol the initiation step involves the reaction of the catalyst precursor (**1**) with CO and the alcohol to give a palladium−carbomethoxy intermediate (**2**) (and a proton), which will generate a polymeric chain starting with an ester end group (Scheme 3a). In this step the dissociation of one molecule of nitrogen ligand also occurs and the free N−N molecule will be very likely involved in a protonation equilibrium. In agreement with the literature,[2] the MALDI analysis indicates that, in methanol, two termination processes occur: the alcoholysis and the β-hydrogen elimination. The alcoholysis requires the nucleophilic attack of methanol on the palladium−acyl intermediate (**3**) and yields a polymeric chain with an

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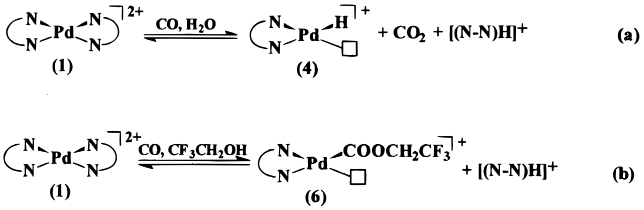
(19) (a) Zuideveld, M. A.; Kamer, P. C. J.; van Leeuwen, P. W. N. M.; Klusener, P. A. A.; Stil, H. A.; Roobeek, C. F. *J. Am. Chem. Soc.* **1998**, *120*, 7977. (b) Margl, P.; Ziegler, T. *J. Am. Chem. Soc.* **1996**, *118*, 7337. (c) Groen, J. H.; Elsevier, C. J.; Vrieze, K.; Smeets, W. J. J.; Spek, A. L. *Organometallics* **1996**, *15*, 3445. (d) Groen, J. H.; Delis, J. G. P.; van Leeuwen, P. W. N. M.; Vrieze, K. *Organometallics* **1997**, *16*, 68. (e) Delis, J. G. P.; Groen, J. H.; Vrieze, K.; van Leeuwen, P. W. N. M.; Veldman, N.; Spek, A. L. *Organometallics* **1997**, *16*, 551.

(20) (a) van Asselt, R.; Gielens, E. E. C. G.; Rülke, R. E.; Elsevier: C. J. *J. Chem. Soc., Chem. Commun.* **1993**, 1203. (b) van Asselt, R.; Gielens, E. E. C. G.; Rülke, R. E.; Vrieze, K.; Elsevier, C. J. *J. Am. Chem. Soc.* **1994**, *116*, 977.

Scheme 4. Initiation Steps in Trifluoroethanol[a]



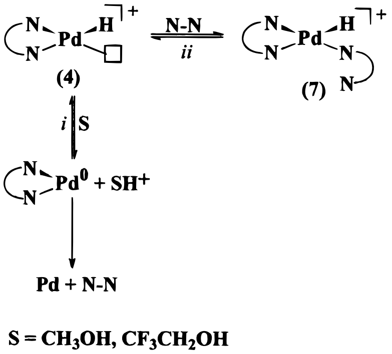
[a] (a) Hydride pathway. (b) Carbotrifluoroethoxy pathway.

ester end group (Scheme 3b1). The β-hydrogen elimination occurs on the palladium−alkyl intermediate (**5**) and yields an unsaturated end group (Scheme 3b2); only the most likely of the two possible unsaturated terminations deriving from a 2,1-insertion of styrene in the growing chain is shown. Both chain-end reactions generate a palladium hydride derivative (**4**), which must be transformed into the active species in order to close the catalytic cycle. In methanol this step is carried out by benzoquinone.[2,3b,13]

The MALDI investigation evidences that, in trifluoroethanol, saturated and unsaturated end groups are present, while no polymeric chains with carbomethoxy groups at both ends are found. Since one end group is always the unsaturated ketone (Scheme 2), which is formed in the termination step, the other chain ends must be originated by at least three different initiation pathways (Scheme 4). In one case, the catalyst precursor (**1**) reacts with carbon monoxide and water yielding the palladium hydride species (**4**) (Scheme 4a). The catalytic data obtained without addition of DMP are in agreement with an activation mechanism involving water. The insertion of the first molecule of styrene into the Pd−H bond can then occur in a primary or a secondary fashion, generating two isomeric saturated end groups. In our case it is not possible to identify which of them is present. The activation of the catalyst precursor through a palladium hydride species was reported for the catalytic system based on hybrid P−N ligands; exclusively the secondary insertion of styrene into the Pd−H bond was observed in that case.[11a] The two other reactions responsible for the activation of the catalyst precursor in trifluoroethanol are the carboalcohoxy pathways, which involve the reaction of **1** with either the fluorinated alcoholic medium (Scheme 4b) or methanol (Scheme 3a), respectively. Methanol is originated by the reaction of dimethoxypropane with water. Due to the lower nucleophilicity of trifluoroethanol compared to methanol, the hydride pathway should become the main initiation process when no DMP is added.

According to the MALDI analysis, the only chain-end reaction occurring in trifluoroethanol is the β-hydrogen elimination, which leads to the palladium hydride intermediate (**4**). In this solvent the alcoholysis reaction does not occur, in agreement with the lower nucleophilicity of TFE compared to MeOH. Moreover, the lack of carboxylic acid end groups indicates that water, present in low concentration when no DMP is used, is not involved in the termination process. Since in trifluoroethanol the copolymerization reaction also proceeds when no benzoquinone is added, the palladium hydride species **4** must be stable enough to allow a new insertion of styrene, thus starting a new polymeric chain with a saturated end group. In methanol, the stability of **4** is quite low, and it easily evolves to palladium(0) and then decomposes to palladium metal (Scheme 5, eq *i*).[2] The lower basicity of trifluoroethanol compared to methanol may be responsible for the increased lifetime of the palladium hydride intermediate (**4**). This intermediate may be also protected from decomposition by the excess of N−N through the equilibrium *ii* with the formation of species **7** (Scheme 5), which may be regarded as a resting state of the catalytic cycle. The [Rh(bpy)$_2$H] species, isoelectronic with **7**, was observed during the catalytic ethanol dehydrogenation promoted by [Rh(bipy)$_2$]Cl.[21]

Scheme 5



Conclusion

In this paper we report that palladium complexes of general formula [Pd(N−N)$_2$][PF$_6$]$_2$ effectively promote CO/styrene copolymerization in trifluoroethanol, in the absence of quinones. The corresponding polyketones are obtained in high yield and with a molecular weight up to 80 000. The high yield is related to the stability of the active species, which is the palladium hydride intermediate **4**, whose lifetime is affected both by the nature of the solvent and by the presence of the mixture of N−N and [(N−N)H]$^+$. The growth of the polymeric chain is the result of the competition between the propagation and the termination steps; a palladium-acyl and a palladium-alkyl intermediate are involved in these two processes. The high values of molecular weight obtained indicate that, due to the suppression of alcoholysis as a termination process, the stability of the Pd-acyl intermediate is greatly enhanced in trifluoroethanol compared to methanol. The β-hydrogen elimination becomes the only effective chain-end reaction, and it is under the control of CO pressure.

Experimental Section

General Comments. Commercial Pd(MeCOO)$_2$ was purchased from Pressure Chemicals and used as received. The bidentate nitrogen-donor chelating ligands, 2,2,2-trifluoroethanol, 2,2-dimethoxypropane (Aldrich), and analytical grade solvents (Baker) were used without further purification for synthetic, spectroscopic, and catalytic purposes. The methanol (Fluka) used for catalytic rections was purified by distillation from magnesium and iodine. Carbon monoxide (CP grade, 99.9%) was supplied by SIAD.

Syntheses. Complexes [Pd(bpy)$_2$][PF$_6$]$_2$ and [Pd(phen)$_2$][PF$_6$]$_2$ were synthesized according to the procedures reported in the literature.[13]

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[21] Morton, D.; Cole-Hamilton, D. J.; Utuk, I. D.; Paneque-Sosa, M.; Lopez-Poveda, M. *J. Chem. Soc., Dalton Trans.* **1989**, 489.

Copolymerization Reaction. The reactions were carried out in a stainless steel autoclave (150 mL), equipped with a Teflon liner, magnetic stirrer, heating mantle, and temperature controller. The complex, styrene, 1,4-benzoquinone (when required), and the solvent were placed in the autoclave, which was then pressurized with CO and heated. After cooling and releasing the residual gas, methanol (200 mL) was added. The copolymer was removed by filtration, washed with methanol, and vacuum-dried.

Molecular Weight Measurement. Before measuring the molecular weight, the CO/styrene polyketones were treated as follows: The copolymer (1.00 g) was stirred in ethyl acetate (50 mL) for 4 h. After filtration it was stirred with diethyl ether (25 mL) for 2 h. The solid was filtered and vacuum-dried.

The copolymers' molecular weights (M_w) and molecular weight distributions (M_w/M_n) were determined by gel permeation chromatography versus polystyrene standards.

The analyses were recorded on a Bruker HPLC (model LC-22) with an Alltech macrosphere GPC 300 Å column and chloroform as a solvent (flow rate 0.5 mL/min).

The CO/styrene copolymers were dissolved as follows: 3 mg of each sample were solubilized with 120 μL of 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP), and then chloroform was added up to 10 mL.

The statistical calculations were performed using the Bruker Chromstar software program.

MALDI/MS Measurement. MALDI mass measurements were performed on a BIFLEX time-of-flight (Bruker Daltonik, Bremen, Germany) instrument, operating in positive reflectron mode. Ions, formed by a pulsed UV laser beam (nitrogen laser, $\lambda = 337$ nm), were accelerated at 19 kV. Pulsed ion extraxtion was done applying to the second grid a voltage of 14 kV for 150 ns.

Dithranol (1,8,9-trihydroxyanthracene) was used as matrix (10 mg/mL in acetone). About 5 mg of each polymer were dissolved in 1 mL of HFIP and about 1 μL of sample solution was deposited on the matrix layer on the sample holder. Mass spectra were obtained averaging 100 laser shots. External mass calibration was made using the $[M + H]^+$ ions of α-cyano-4-hydroxycinnamic acid (m/z 225.08) and ACTH 1−17 (m/z 2094.96).

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