Palladium-Promoted Carbon Monoxide/Ethylene/Styrene Terpolymerization Reaction: Throwing Light on the Different Reactivity of the Two Alkenes

by **Jérôme Durand**[a])[1]), **Alessandro Scarel**[a]), **Barbara Milani***[a]), **Roberta Seraglia**[b]), **Serafino Gladiali**[c]), **Carla Carfagna**[d]), and **Barbara Binotti**[d])

[a]) Dipartimento di Scienze Chimiche, Università degli Studi di Trieste, Via Licio Giorgieri 1, I-34127 Trieste (e-mail: milani@dsch.units.it)
[b]) CNR, Istituto di Scienze e Tecnologie Molecolari Sez. di Padova, Corso Stati Uniti 4, I-35127 Padova
[c]) Dipartimento di Chimica, Università di Sassari, Via Vienna 2, I-07100 Sassari
[d]) Istituto di Scienze Chimiche, Università di Urbino, Piazza Rinascimento 6, I-61029 Urbino

Dedicated to Professor *Giambattista Consiglio* for his outstanding contribution to the development of asymmetric polymerization.

The catalytic behavior of dicationic bis-chelated Pd^{II} complexes, $[Pd(N{-}N)_2][PF_6]_2$, in the CO/ethylene/styrene terpolymerization reaction is studied in detail. The bidentate N-donor ligands were chosen among 2,2′-bipyridine (**1**), 1,10-phenanthroline (**3**), their symmetrically substituted derivatives **2**, **4**, and **5**, and 3-alkyl-substituted 1,10-phenanthrolines **6**–**10**. The effect of several parameters (like temperature, CO/ethylene pressure, styrene content, reaction time) was investigated and related to the productivity of the catalytic system, to the relative content of the two olefins in the polymeric chains, and to the molecular mass of the synthesized polyketones. The presence of 1,4-benzoquinone was necessary to reach productivities as high as 16 kg of terpolymer (TP) per gram of Pd. ^{13}C-NMR spectroscopy was useful to characterize the distribution of the two repetitive units along the polymer chain. Terpolymers with prevailingly isolated CO/styrene units in CO/ethylene blocks as well as terpolymers with CO/styrene and CO/ethylene blocks were obtained by varying the reaction conditions. Detailed MALDI-TOF-MS analysis was performed on the CO/ethylene/styrene terpolymers for the first time, and it allowed us to characterize the end groups of the terpolymer chains. The presence of different chain end groups was found to be related to the initial amount of the two alkenes, thus suggesting that different reactions are involved in the initiation and termination steps of the terpolymerization catalytic cycle.

Introduction. – The copolymerization of carbon monoxide with alkenes affords perfectly alternated polyketones, a family of polymers that is the subject of intense research [1]. This led to the development of very efficient catalytic systems based on palladium complexes containing different types of ligands [2]. While chelating diphosphines are the ligands of choice for the copolymerization of aliphatic alkenes such as ethylene (=ethene) or propylene (=prop-1-ene), in the case of aromatic substrates such as styrene (=ethenylbenzene), bidentate N–N or P–N heterodonor derivatives are, with few exceptions [3], the best-suited ligands [4].

Though polyketones became a commercial reality thanks to the terpolymeric material obtained from CO, ethylene, and propylene (*Carilon*® from *Shell*, and *Ketonex*®

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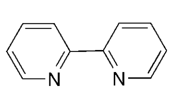
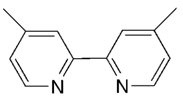
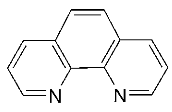
[1]) Current address: Laboratoire Hétérochimie Fondamentale et Appliquée, Université Paul Sabatier, UMR CNRS 5069, Bâtiment 2R1, 118, route de Narbonne, F-31062 Toulouse Cedex 9.



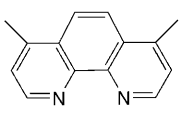
1 bipy



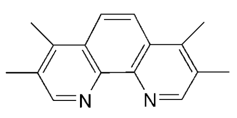
2 dmbipy



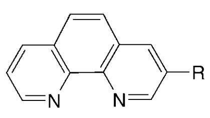
3 phen



4 dmphen



5 tmphen



6 R = Me **9** R = ^{i}Pr
7 R = Et **10** R = MeCH$_2$CH(Me)
8 R = Bu

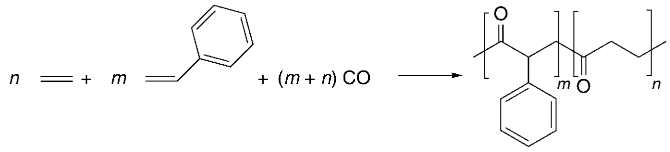
from *BP*), terpolymerization reactions have attracted much less attention than copolymerization.

As most of the studies on terpolymerization have been focussed on the reaction of aliphatic alkenes, [Pd(diphosphine)] complexes have been consistently used as catalysts [5]. Only one report has appeared thus far on the terpolymerization of CO with two aromatic alkenes promoted by [Pd(phenanthroline)] complexes [6]. As a matter of fact, in comparison with the more simple CO/ethylene copolymerization, the terpolymerization of CO with one aliphatic and one aromatic olefin allows for a higher degree of flexibility in the choice of the catalytic system and, in addition to chelating N–N [7], P–N [8], or P–OP bidentate ligands [9], also Pd-complexes with chelating diphosphines catalyze this reaction [10].

Two years ago, we reported dicationic, bis-chelated Pd^{II} complexes with 3-alkyl-substituted 1,10-phenanthrolines (3-R-phen) as catalysts for the synthesis of syndiotactic CO/ethenylarene polyketones. Productivities as high as 8 kg CP/g Pd (kg CP/g Pd = kilograms of copolymer per gram of palladium) and of 12 kg CP/g Pd for styrene and *p*-methylstyrene (= 1-ethenyl-4-methylbenzene), respectively, with M_w values around 300,000, have been attained without any additional co-reagent or co-catalyst [11].

In the present paper, we report some results on the catalytic behavior of the dicationic, bis-chelated Pd^{II} complexes [Pd(N–N)$_2$][PF$_6$]$_2$ in the terpolymerization of CO with ethylene and styrene (*Scheme 1*). The N–N ligands were chosen among 2,2′-bipyridine (bipy; **1**), 1,10-phenanthroline (phen; **3**) and their symmetrically and nonsymmetrically substituted derivatives **2** and **4**–**10**.

Scheme 1. *Terpolymerization of Carbon Monoxide with Ethylene and Styrene*



Results and Discussion. – *Terpolymerization Reactions.* The terpolymerization reactions were carried out in 2,2,2-trifluoroethanol (CF$_3$CH$_2$OH), a solvent that has been previously shown to be particularly appropriate for this kind of reaction [12]. Also 1,4-benzoquinone (BQ) was added to the reaction mixture, and a 1:1 mixture of CO/ethylene was used.

A first series of experiments was run with $[Pd(\mathbf{1})_2][PF_6]_2$ as catalyst precursor to study the influence of the different parameters on the performance of the catalytic system. Temperature has a pronounced effect on the catalytic activity (*Table 1*). While an increase of 20°, from 50° to 70°, led to an improvement of the productivity of more than one order of magnitude up to 10 kg TP/g Pd (TP = terpolymer), a further increase of 10° (up to 80°) resulted in a decrease. The loss of productivity at 80° was due to catalyst decomposition to inactive Pd metal; this effect was already evidenced at 75° by the grey color of the terpolymer, while no decomposition was observed up to 70°. This last temperature was then chosen for the following experiments.

Table 1. *CO/Ethylene/Styrene Terpolymerization: Influence of Reaction Temperature.* Precatalyst: $[Pd(\mathbf{1})_2][PF_6]_2$[a]).

T [°]	g TP	kg TP/g Pd	% Styrene[b])
50	0.2	0.4	37
60	0.7	1.3	43
70	5.4	10.2	42
75	5.5	10.3	41
80	3.5	6.5	47

[a]) Reaction conditions: $n_{Pd} = 5 \cdot 10^{-6}$ mol, solvent CF_3CH_2OH (35 ml), styrene (15 ml), $P_{CO/ethylene}$ 30 bar, CO/ethylene 1:1; reaction time 6 h, [BQ]/[Pd] = 40 (BQ = 1,4-benzoquinone). [b]) Styrene content in the terpolymer as determined by ^{1}H-NMR (see text).

Temperature also had a slight influence on the content of styrene (determined by ^{1}H-NMR, see below) in the polymeric materials. Raising the temperature from 50° to 80° resulted in an increase of the share of the aromatic olefin from 37 to 47% (*Table 1*), indicating that higher reaction temperatures favor the insertion of styrene with respect to ethylene. In agreement with [12a], an increase of temperature caused a decrease of the molecular mass of the polymer. For example, they dropped from 20,000 to 13,000 in going from 60° to 80°.

The influence of the initial amount of styrene was then studied keeping constant the total volume of the liquid phase to work always at the same catalyst concentration. The increase of the amount of styrene caused an increase in the productivity, up to 12 kg TP/g Pd (*Fig. 1*) and, at the same time, the share of styrene in the polymer chain increased up to 43% of the inserted alkenes (*Fig. 1*). The increase of styrene content does not affect that much the molecular-mass values of the terpolymers, which remained around 25,000.

The influence of reaction time was studied under the same conditions, with an initial amount of styrene of 15 ml (*Fig. 2*). In the range 0–8 h, the productivity clearly increased in a proportional way with time, whereas prolonging the reaction time up to 24 h resulted in a very modest increase in terms of productivity, thus showing that a plateau was reached due to the decomposition of the active species, as evidenced by the black color of the obtained polymer (*Fig. 2*). Moreover, a slight decrease of

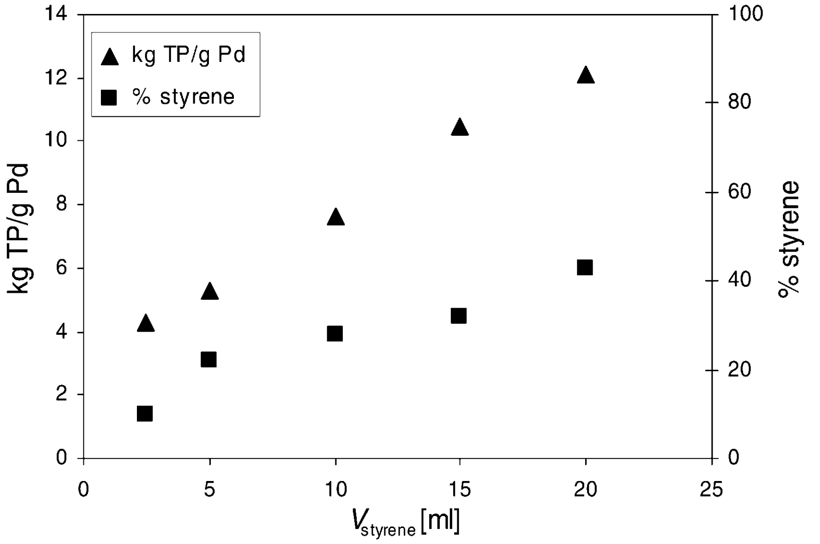


Fig. 1. *CO/Ethylene/styrene terpolymerization: influence of the initial amount of styrene.* Precatalyst: $[Pd(\mathbf{1})_2][PF_6]_2$. Reaction conditions: $n_{Pd} = 5 \cdot 10^{-6}$ mol, solvent CF_3CH_2OH ((50 – $V_{styrene}$) ml), $P_{CO/ethylene}$ 30 bar, CO/ethylene 1:1, [BQ]/[Pd] 40:1, 70°, 7 h. The % of styrene represents the styrene content in the terpolymer as determined by ^{1}H-NMR (see text).

the styrene content in the terpolymers obtained after longer reaction times was observed, suggesting that styrene insertion is more favored at the early stage of the reaction. At longer reaction times, a decrease was also observed for the molecular mass of the polymers (from 31,000 after 3 h to 24,000 after 24 h).

Different bidentate N-donor ligands were tested in the terpolymerization under optimized reaction conditions. First, we explored the catalytic behavior of Pd-species containing the symmetrically disubstituted 2,2′-bipyridine or 1,10-phenanthroline ligands **2** or **4** and **5**, respectively. In analogy with the CO/styrene copolymerization reactions, the catalyst containing ligand **1** showed a higher activity than the phenanthroline counterpart **3** (*Table 2*). The introduction of Me substituents at the ligands induced a decrease of productivity, as previously reported in the case of the copolymerization reactions (*Table 2*) [7a][11][12b][13]. However, the origin of this effect is different for the bipy and the phen ligands. In the case of the dmbipy (**2**)-containing catalyst, the loss of productivity is due to the lifetime of the catalyst, which for the dmbipy species is shorter than for the bipy derivative, as evidenced by the formation of Pd metal. At variance, in the case of dmphen or tmphen ligands **4** or **5**, respectively, no decomposition was noticed, thus indicating that the decrease in productivity is related to the inertness of the precatalyst rather than to the instability of the catalyst. This conclusion finds further support in quite recent results which show that, in the CO/styrene copolymerization promoted by mono-chelated complexes [Pd(Me)(MeCN)(N–N)][PF_6], a clear decrease of the rate of CO uptake without any catalyst decomposition is observed in moving from **3** to **4** as ligands [14].

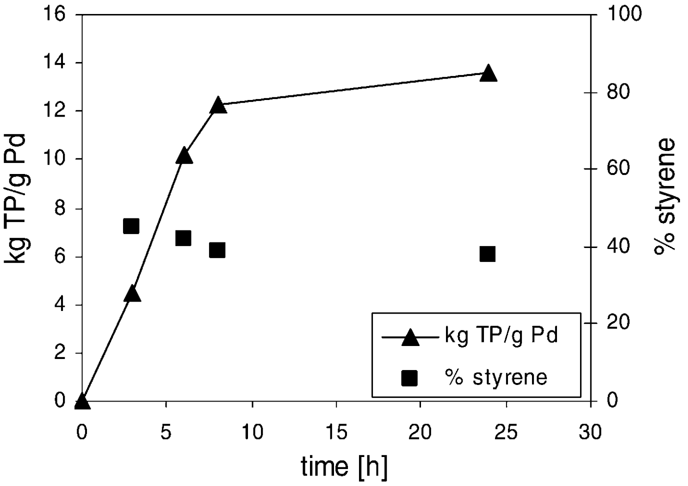


Fig. 2. *CO/Ethylene/styrene terpolymerization: influence of the reaction time.* Precatalyst: $[Pd(\mathbf{1})_2][PF_6]_2$. Reaction conditions: $n_{Pd} = 5 \cdot 10^{-6}$ mol, solvent CF_3CH_2OH (35 ml), styrene (15 ml), $P_{CO/ethylene}$ 30 bar, CO/ethylene 1:1, [BQ]/[Pd] 40:1, 70°. The % of styrene represents the styrene content in the terpolymer as determined by ^{1}H-NMR (see text).

Both for the bipyridine and the phenanthroline ligands, an increase of the basicity favors, albeit only slightly, the insertion of styrene in the growing chain (*Table 2*). For the polymers obtained with phenanthroline ligands, the molecular-mass values are in the range 23,000–27,000. The introduction of Me substituents causes a shortening of the chain length, as evidenced in going from **4** (M_w 27,000) to **5** (M_w 23,000).

Table 2. *CO/Ethylene/Styrene Terpolymerization: Influence of the Chelating Ligand.* Precatalyst: $[Pd(N\text{–}N)_2][PF_6]_2$[a]).

N–N	Abbrev.	g TP	kg TP/g Pd	% Styrene[b])
1	bipy	5.4	10.2	42
2	dmbipy	1.3	2.4	48
3	phen	3.2	5.9	50
4	dmphen	2.2	4.2	48
5	tmphen	1.8	3.3	56

[a]) Reaction conditions: $n_{Pd} = 5 \cdot 10^{-6}$ mol; solvent CF_3CH_2OH (35 ml), styrene (15 ml), $P_{CO/ethylene}$ 30 bar, CO/ethylene 1:1; *T* 70°, reaction time 6 h, [BQ]/[Pd] = 40. [b]) Styrene content in the terpolymer as determined by ^{1}H-NMR (see text).

The influence of the addition of benzoquinone to the catalytic system was studied in the terpolymerization reactions catalyzed by $[Pd(\mathbf{3})_2][PF_6]_2$. As reported in the case of the copolymerization reactions [12b], a decrease of the amount of oxidant reduces the productivity of the corresponding catalytic system (*Fig. 3*). It is remarkable that, in the presence of up to 20 equiv. of benzoquinone, even after a rather short reaction time (6 h), decomposition of the catalyst to Pd metal was observed. This contrasts with

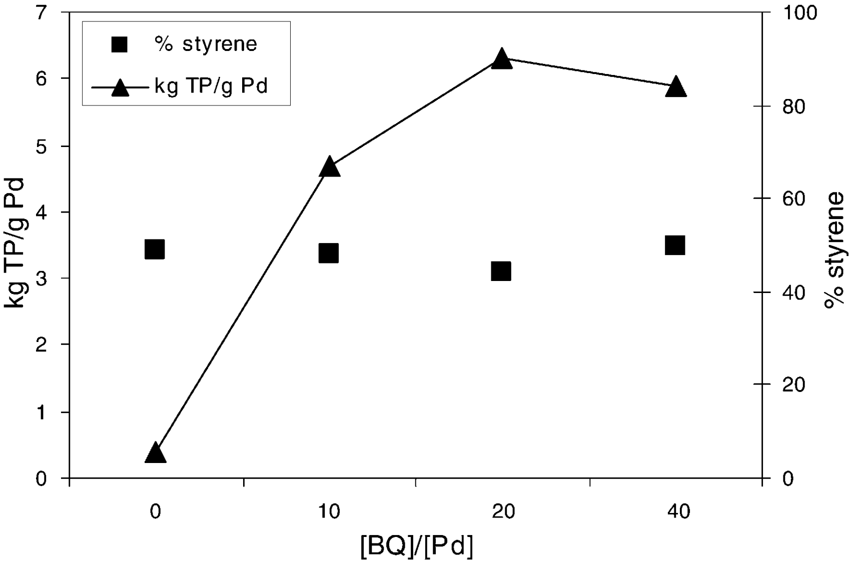


Fig. 3. *CO/Ethylene/styrene terpolymerization: influence of the amount of benzoquinone (BQ).* Precatalyst: $[Pd(\mathbf{3})_2][PF_6]_2$. Reaction conditions: $n_{Pd} = 5 \cdot 10^{-6}$ mol, solvent CF_3CH_2OH (35 ml), styrene (15 ml), $P_{CO/ethylene}$ 30 bar, CO/ethylene 1:1, 70°, 6 h. The % of styrene represents the styrene content in the terpolymer as determined by ^{1}H-NMR (see text).

our previous observation that, in the CO/styrene copolymerization, these same catalysts retain their activity for quite a long time (up to 96 h) without any visible sign of decomposition, even in the absence of the oxidant [11][12b]. On the other hand, when the same precatalysts were tested in the CO/ethylene copolymerization, benzoquinone was necessary to avoid fast catalyst decomposition [11]. This analysis demonstrates that the aliphatic olefin has a dramatic negative effect on the catalyst stability, and this effect is not completely overcome by the presence of the aromatic alkene.

The effect of pressure of the CO/ethylene mixture was investigated by using $[Pd(\mathbf{3})_2][PF_6]_2$ as precatalyst. The highest activity was obtained with an initial pressure of 20 bar (*Fig. 4*). The decrease of productivity observed at 30 bar might be related to the inhibiting effect of CO, since no Pd metal was formed under these reaction conditions. As expected, the relative amount of styrene inserted into the polymer chain increased on decreasing the CO/ethylene pressure. The CO/ethylene pressure exerts a significant influence on the molecular mass of the polymers, which dropped from 27,000 to 2,900 when the pressure decreased from 30 to 10 bar. At 20 bar, the intermediate value of 11,000 was obtained.

The study of the influence of the nature of the chelating ligand was extended to the nonsymmetric 3-alkyl-1,10-phenanthrolines **6**–**10** (*Table 3*). The introduction of a small substituent (Me or Et, ligands **6** and **7**) at the phenanthroline backbone led to a decrease of the productivity of the corresponding Pd complexes, whereas with slightly larger groups, such as the C_4H_9 substituents, *i.e.*, ligands **8** and **10**, a slight improvement of the productivity, up to 16.4 kg TP/g Pd, was observed. It is interesting to compare

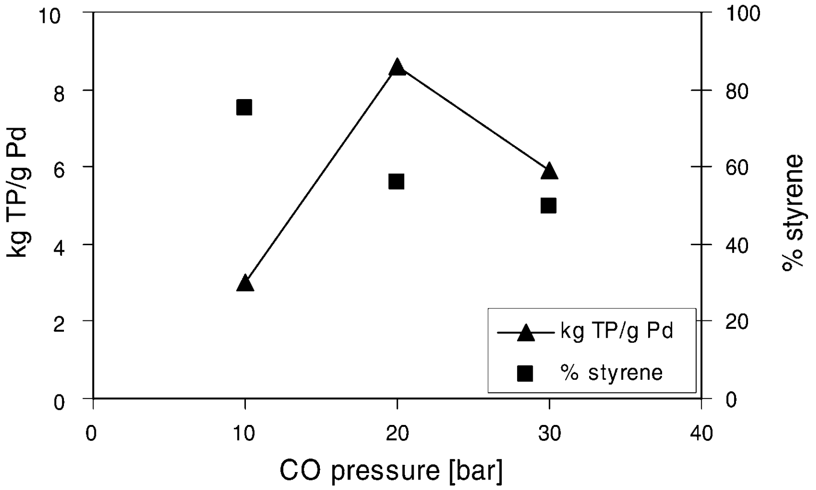


Fig. 4. *CO/Ethylene/styrene terpolymerization: influence of the CO/ethylene pressure.* Precatalyst: $[Pd(\mathbf{3})_2][PF_6]_2$. Reaction conditions: $n_{Pd} = 5 \cdot 10^{-6}$ mol, solvent CF_3CH_2OH (35 ml), styrene (15 ml), CO/ethylene 1:1, [BQ]/[Pd] 40:1, 70°, 6 h. The % of styrene represents the styrene content in the terpolymer as determined by ^{1}H-NMR (see text).

these results with those obtained in the case of the two copolymerization reactions (CO/ethylene *vs.* CO/styrene). Compared with unsubstituted phenanthroline, ligands **6** and **7** showed a similar behavior in all the reactions tested, giving a lower or similar productivity [11]. Ligands **9**–**10** generated more active catalysts in both the CO/styrene copolymerization and the CO/ethylene/styrene terpolymerization, while almost no effect of the substituent was found in the CO/ethylene copolymerization [11].

In all cases with 3-alkyl-substituted ligands, the insertion of styrene is favored over that of ethylene (*Table 3*). This is in keeping with the behavior previously observed in the copolymerizations of CO/styrene and CO/ethylene in the presence of 3-R-phen catalysts. Molecular masses of the terpolymers obtained with these 3-R-phen ligands are almost unchanged and range in between 21,000 and 27,000. This contrasts with the

Table 3. *CO/Ethylene/Styrene Terpolymerization: Influence of the Nature of the Alkyl Substituent.* Precatalyst: $[Pd(3\text{-R-phen})_2][PF_6]_2$[a]).

3-R-phen	g TP	kg TP/g Pd	% Styrene[b])
3 phen	7.0	13.2	40
6 3-Me-phen	6.0	11.3	50
7 3-Et-phen	6.3	11.9	50
8 3-Bu-phen	8.6	16.2	50
9 3-^{i}Pr-phen	7.5	14.0	56
10 3-^{s}Bu-phen	8.7	16.4	52

[a]) Reaction conditions: $n_{Pd} = 5 \cdot 10^{-6}$ mol, solvent CF_3CH_4OH (35 ml), styrene (15 ml), $P_{CO/ethylene}$ 30 bar; CO/ethylene 1:1, [BQ]/[Pd] 40:1, 70°, 24 h. [b]) Styrene content in the terpolymer as determined by ^{1}H-NMR (see text).

CO/styrene copolymerization [11], and seems to indicate a major role of the aliphatic alkene in the determination of the length of the polymeric chains.

The effect of the initial amount of styrene, studied with precatalyst $[Pd(\mathbf{8})_2][PF_6]_2$, showed that the highest productivity was reached with an initial amount of 15 ml of the aromatic alkene (*Fig. 5*). Working in neat styrene, *i.e.*, in the absence of CF_3CH_2OH as solvent, led to a very low activity, but afforded a polymer with an even higher content of styrene. This low catalytic activity is associated again with the decomposition of the active species, thus confirming the stabilizing effect of the fluorinated solvent. As in the case of the experiments catalyzed by $[Pd(\mathbf{1})_2][PF_6]_2$ (*Fig. 1*), the styrene content in the terpolymer increases with the initial amount of aromatic alkene present in the catalytic system. Nevertheless, this increase is matched by a decrease of molecular-mass values from 36,000 (at 33% of styrene) to 19,000 (at 79% of styrene).

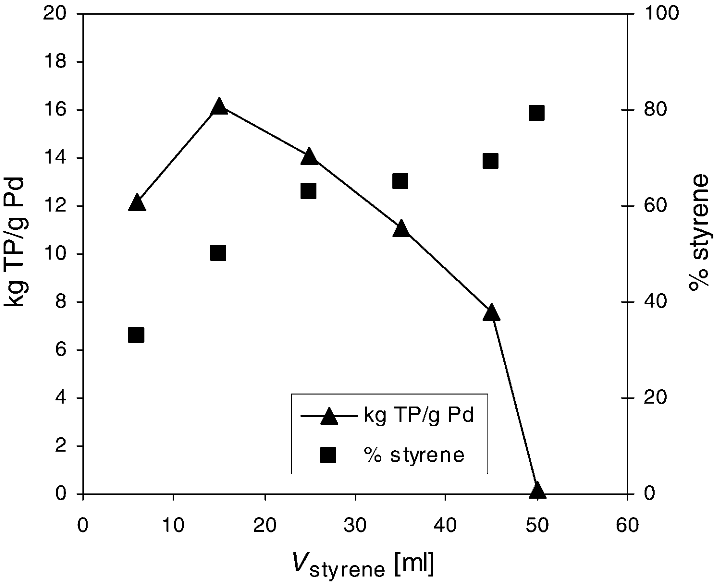


Fig. 5. *CO/Ethylene/styrene terpolymerization: influence of the initial amount of styrene.* Precatalyst: $[Pd(\mathbf{8})_2][PF_6]_2$. Reaction conditions: $n_{Pd} = 5 \cdot 10^{-6}$ mol, solvent CF_3CH_2OH ($(50 - V_{\text{styrene}})$ ml), $P_{\text{CO/ethylene}}$ 30 bar, CO/ethylene 1:1, [BQ]/[Pd] 40:1, 70°, 24 h. The % of styrene represents the styrene content in the terpolymer as determined by ^{1}H-NMR (see text).

Some gas-uptake measurements were performed during the terpolymerization catalyzed by $[Pd(\mathbf{8})_2][PF_6]_2$ with two different amounts of 1,4-benzoquinone (*Fig. 6*). At [BQ]/[Pd] 40:1, a linear relationship holds between the CO uptake and the time in the first 8 h. Then, the plot profile changes suddenly due to the decomposition of the active species. When the [BQ]/[Pd] ratio was raised from 40 to 80, no effect on the rate of CO uptake was observed in the first 16 h, in agreement with literature data on CO/styrene copolymerization carried out either in MeOH [15] or in CF_3CH_2OH [14]. The amount of the oxidant remarkably affects the reaction time at which the terpolymerization reaction stops, and it is increased from 8 to 16 h by doubling the amount of benzoquinone present. This result clearly indicates that the catalyst lifetime is strictly

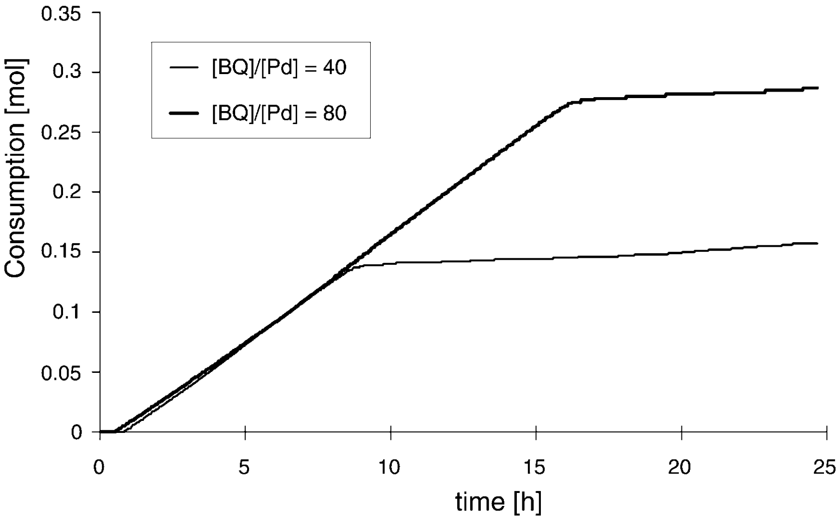


Fig. 6. *Gas uptake in the course of the CO/ethylene/styrene terpolymerization catalyzed by* $[Pd(\mathbf{8})_2][PF_6]_2$. Reaction conditions: $n_{Pd}=5\cdot10^{-6}$ mol, solvent CF_3CH_2OH (35 ml), styrene (15 ml), $P_{CO/ethylene}$ 30 bar, CO/ethylene 1:1, 70°.

related to the [BQ]/[Pd] ratio and that, when the benzoquinone is completely consumed, the Pd catalyst decomposes irreversibly. Very recently, we have found that in the CO/styrene copolymerization promoted by phenanthroline-containing catalysts at a [BQ]/[Pd] ratio of 5:1, the CO uptake does not drop for at least 96 h, and that no catalyst decomposition occurs [14]. This comparison confirms that, in the presence of the aliphatic alkene, a large excess of benzoquinone is required for high productivities to be achieved. Overall, these data point out the different roles played by the aliphatic and the aromatic alkene in terpolymerizations.

Polyketone Characterization. All the solids obtained in the catalytic experiments described here are perfectly alternated polyketones and were characterized by ^{1}H- and ^{13}C-NMR spectroscopy in solution and by MALDI-TOF mass spectrometry. The first evidence that these solids are terpolymers and not a mixture of the corresponding copolymers derives from their complete solubility in $CHCl_3$, in contrast to the insolubility of the CO/styrene and CO/ethylene polyketones in the same solvent. Therefore, the NMR characterization was performed by recording the spectra in $CDCl_3$.

In the ^{1}H-NMR spectra, the three signals present in the aliphatic region (see *Exper. Part*) are the most informative. In agreement with literature data [7f] [8a], their integration allows the determination of the relative amounts of the two olefins present in the terpolymers.

In the ^{13}C-NMR spectra, the signals of the carbonyl groups are observed at δ 207–208, thus confirming that the polymers isolated are polyketones. In the aliphatic region of the spectra, different signals can be observed, and they can be assigned by comparison with the spectra of the corresponding CO/olefin copolymers (*Fig. 7*). Hence, the signals at δ 54 correspond to the CH groups of the styrene-derived units, their CH_2 groups being observed in the range δ 42–46, and the signals of the ethyl-

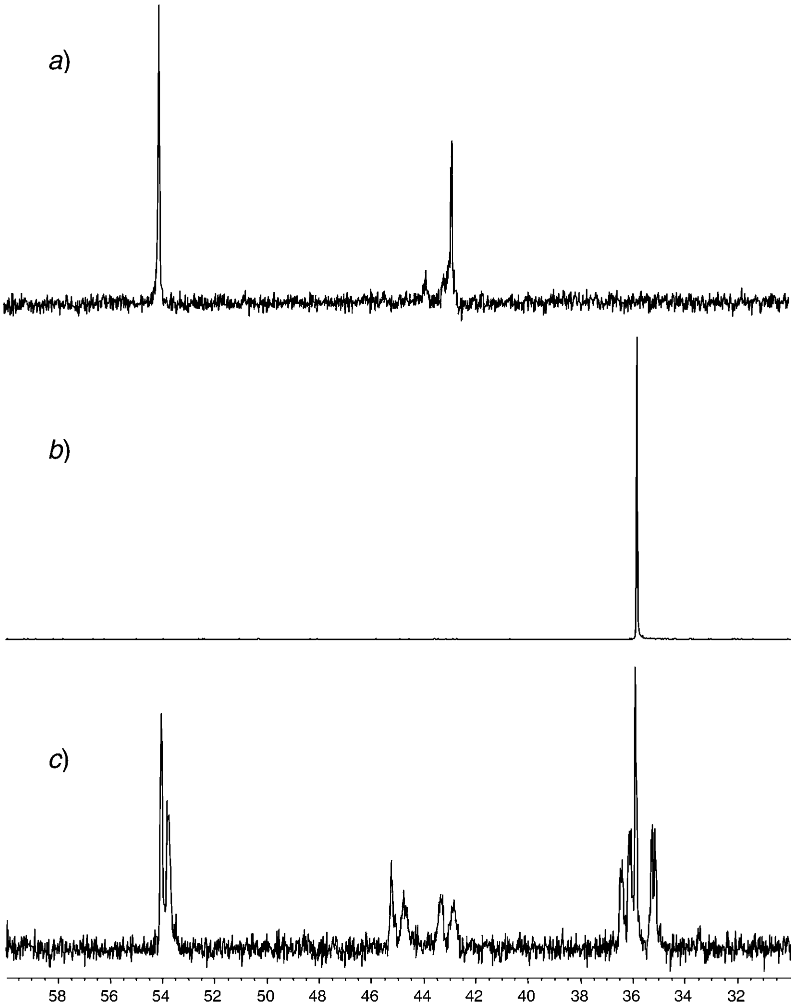


Fig. 7. *Aliphatic range of the* ^{13}*C-NMR spectra* ($CDCl_3$) *of* a) *a CO/styrene copolymer,* b) *a CO/ethylene copolymer, and* c) *a CO/ethylene/styrene terpolymer*

ene-derived C-atoms appear at δ 35–37. Each group is composed of different signals, unlike what is observed for the corresponding copolymers, due to the different chemical environments possible for each repetitive unit. This allows one to confirm that the polymeric material is not simply a mixture of the two copolymers, but has really a terpolymer structure. In agreement with the characterization reported for the CO/ethylene/*p*-(*tert*-butyl)styrene terpolymers [7f], the CH_2 group of the inserted styrene monomer generates the most significant signal for the structural analysis (*Fig. 8*). The comparison of this region of the spectrum for terpolymers of different composition shows that, in the case of the polymer containing 52% of styrene, four signals, *A*, *B*, *C*, and *D*, having roughly the same intensity, are present. Their relative intensities vary with the

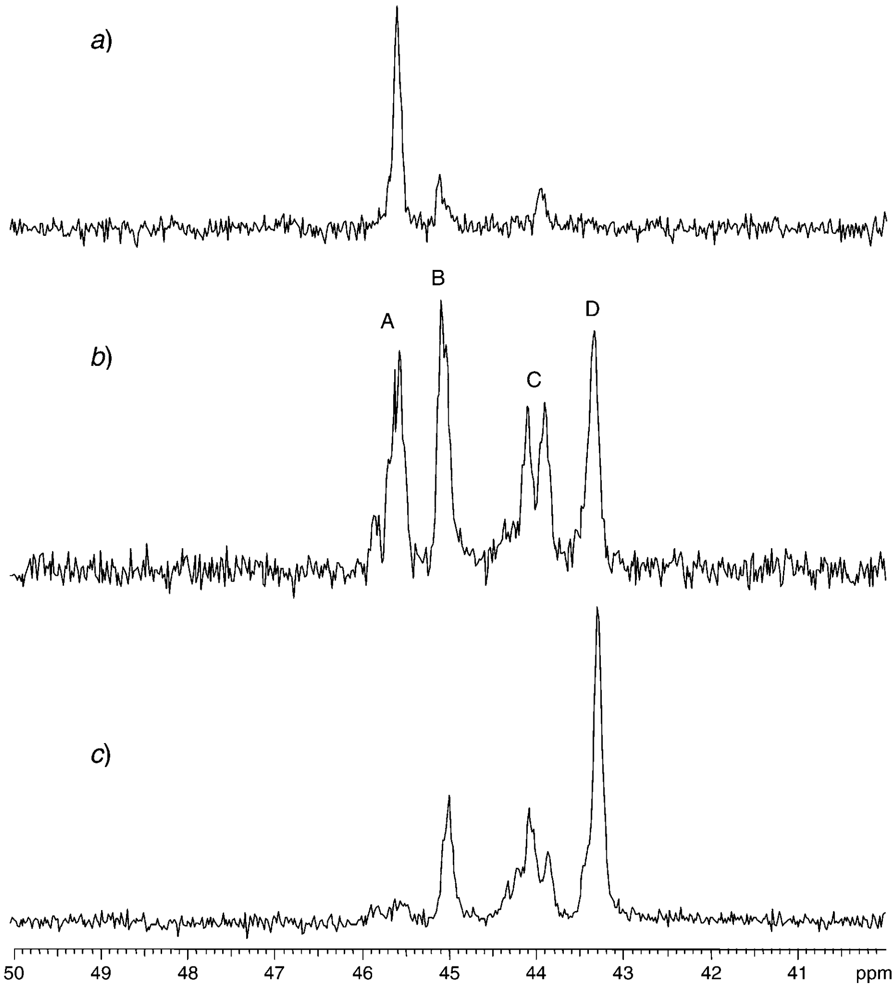


Fig. 8 *Range of the styrene-derived CH_2 groups in the ^{13}C-NMR spectra* ($CDCl_3$) *of CO/ethylene/styrene terpolymers containing* a) *22% of styrene*, b) *52% of styrene, and* c) *79% of styrene*

content of styrene in the polymeric chain. Hence, for a polymer of low styrene content, only three resonances are observed, the most intense, signal *A*, is at higher frequency and, on the basis of the reported data [8a], is attributed to a CO/styrene unit surrounded by CO/ethylene repetitive units. In the case of a high styrene content, signal *A* is not observed anymore, and the most intense is now the resonance at lower frequency, signal *D*, which is attributed to a CO/styrene unit between at least two other CO/styrene units (*Fig. 8*). Interestingly, the relative intensity of the four signals is also dependent on the nature of ligand used (*Table 4*). For terpolymers having the same content of styrene (*ca.* 50%), signal *A* is the most intense when **1**, **3**, **4**, or **6** are used as ligands, showing, thus, that in these cases, the polymer is mainly constituted of CO/ethylene blocks containing isolated CO/styrene units. However, this is not

Table 4. *Influence of the Chelating Ligands on the Relative Intensities of the Styrene-Derived CH_2 Groups in the ^{13}C-NMR Spectra of the Terpolymers*[a])

Ligand	% Styrene	Relative intensity [%] of the four signals			
		A	B	C	D
1 bipy	48	34	24	25	17
3 phen	50	33	25	26	16
4 dmphen	48	34	26	21	19
6 3-Me-phen	50	36	24	24	16
7 3-Et-phen	50	26	25	28	21
9 3-^{i}Pr-phen	56	25	23	30	22
8 3-Bu-phen	50	26	27	28	19
10 3-*s*Bu-phen	52	25	24	28	23

[a]) Spectra recorded in $CDCl_3$ at room temperature.

observed in the case of all the other 3-substituted phenanthrolines tested, *i.e.*, ligands **7**–**10**, where all the four signals are present in similar proportions (*Table 4*). In the latter case, the amount of isolated CO/styrene units in the terpolymers is, thus, lower.

To go in detail into the analysis of the terpolymers, three samples with a different content of the two alkenes were prepared on a larger scale by using the double volume for the liquid phase and three times the quantity of Pd catalyst with respect to the experiments reported above (*Table 5*). Three CO/ethylene/styrene terpolymers, namely TP1, TP2, and TP3, differing in the relative content of the two alkenes, were characterized by MALDI-TOF-MS for the first time. On going from sample TP1 to TP3, the amount of styrene in the polymer chain decreases from 77 to 15%, with the corresponding increase of the amount of ethylene as complement to 100%. The comparison of the three mass spectra (*Fig. 9*) evidences that their complexity is strongly related to the styrene content in the polymer chain. Thanks to the knowledge acquired by studying the CO/styrene/*p*-methylstyrene terpolymers [6], it was possible to interpret the spectra of the CO/ethylene/styrene terpolymers by considering a cluster as a group of peaks with the same $(m+n)$ value, where m and n are the number of CO/styrene and CO/ethylene units present in the chain, respectively. In contrast to what was previously reported by us for the MALDI-TOF-MS analysis of the CO/styrene/*p*-methylstyrene terpolymers [6], the spectra of the CO/ethylene/styrene terpolymers are not

Table 5. *CO/Ethylene/Styrene Terpolymerization: Influence of the Initial Amount of Styrene*[a])

Terpolymer	Catalyst	Styrene [ml]	% Styrene[b])
TP1	$[Pd(\mathbf{8})_2][PF_6]_2$	100 ml	77
TP2	$[Pd(\mathbf{8})_2][PF_6]_2$	30 ml	60
TP3	$[Pd(\mathbf{1})_2][PF_6]_2$	5 ml	15

[a]) Reaction conditions: $n_{Pd} = 15 \cdot 10^{-6}$ mol, solvent CF_3CH_2OH ($(100 - V_{styrene})$ ml), $P_{CO/ethylene}$ 30 bar, CO/ethylene 1:1, [BQ]/[Pd] 40:1, 70°, 24 h. [b]) Styrene content in the terpolymer as determined by ^{1}H-NMR (see text).

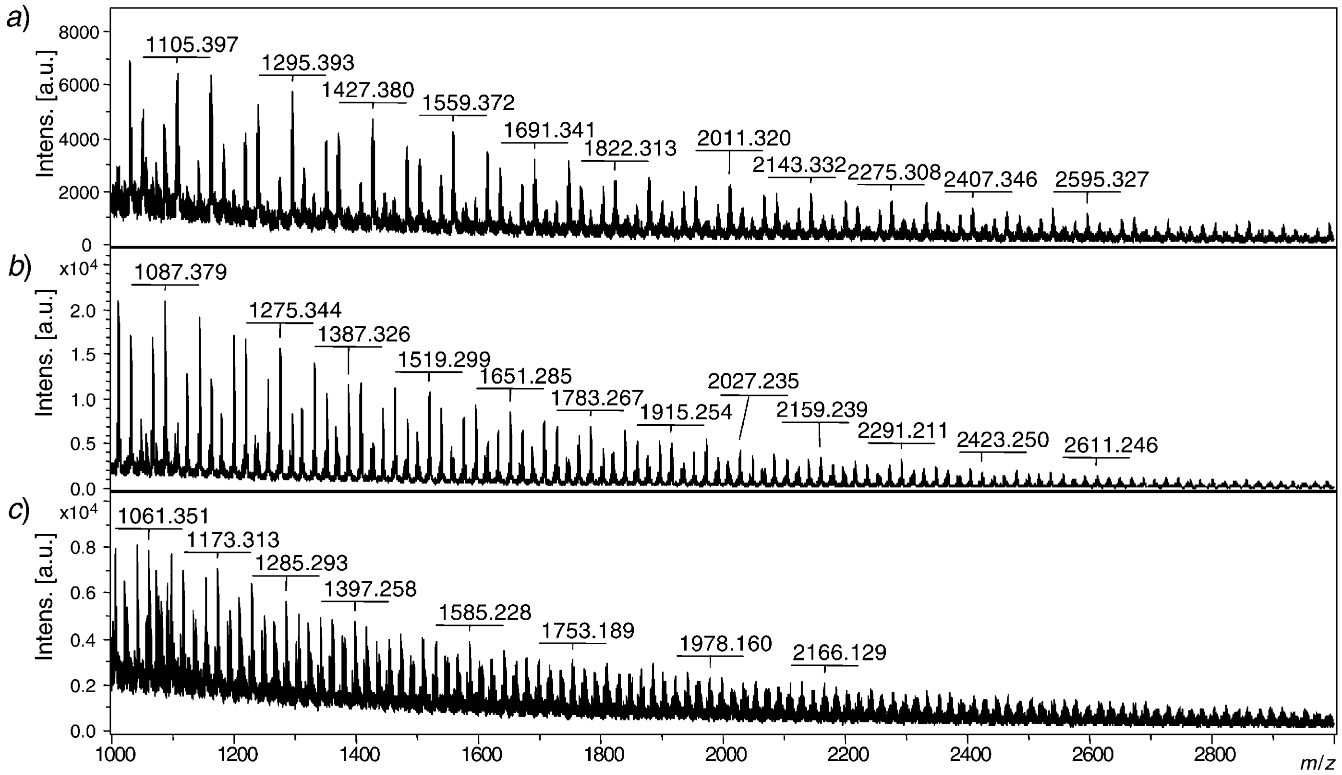


Fig. 9. *MALDI-TOF Mass spectra of CO/ethylene/styrene terpolymers with different ethylene/styrene ratio*: a*) TP1* (77% styrene, 23% ethylene), b*) TP2* (60% styrene, 40% ethylene), *and* c*) TP3* (15% styrene, 85% ethylene)

characterized by the presence of well-separated clusters, but each cluster is spread on a wide range of m/z values, and the peaks of each cluster are mixed up. This is due to the difference in mass of the CO/styrene and CO/ethylene repetitive units, which is 76 Da.

Focusing our attention on the same m/z range (m/z 1200–1600), clear differences in the mass spectra of the three terpolymers TP1–TP3 can be observed (*Figs. 10* and *11*). In particular, while the spectra of terpolymers TP1 and TP2 share some peaks, the spectrum of TP3 is completely different. In the case of the TP1 terpolymer, MALDI-TOF-MS analysis reveals the presence of two kinds of polymer chains differing by the end groups: one (polymer chain *a*) with a saturated alkyl moiety (derived from insertion of the alkene into the Pd–H species) and an unsatured alkyl moiety (originated from β-H elimination) as end groups, and the other one (polymer chain *b*) with a saturated alkyl moiety and a carboxylic acid residue as end groups (*Fig. 12*). Chain *b* features an additional carbonyl group resulting from a double carbonylation reaction followed by chain termination. This kind of termination has been recently observed by us in CO/styrene polyketones synthesized by (4,4′,5,5′-tetrahydro-2,2′-bioxazol)palladium complexes [16]. It is not possible to distinguish whether the alkyl end groups arise from styrene or ethylene. Each oligomer chain is detected as cationized species, preferentially with lithium, as already observed for the CO/styrene/*p*-methylstyrene terpolymer, even if no cationizing agent was added to the terpolymer solution.

As it can be seen in *Fig. 10,a*, the peaks due to the different polymer chains *a* and *b* with different $(m+n)$ values (labelled a_{m+n} and b_{m+n} in the figure) are mixed up, but they can be easily distinguished. Due to the presence of different cations, some clusters cannot be univocally attributed to only one kind of polymer chain, but to two or three chains differing for both the cation and the $(m+n)$ value. For instance, the cluster formed by peaks at m/z 1275, 1351, 1427, and 1503 could correspond both to a terpolymer chain with $(m+n)=13$, cationized with lithium, and to a chain with $(m+n)=10$, cationized with sodium.

In the case of TP2 terpolymer (*Fig. 10,b*), containing a lower percentage of styrene (60%), only one polymer chain is individuated, corresponding to polymer chain *a* of TP1. The end groups of the polymer chain are the saturated and unsaturated alkyl residues, as previously described. The peaks due to polymer chain *b* are completely absent. Also in this case, some cluster cannot be univocally attributed to a single ionic species due to the presence of different cations: *i.e.*, the cluster formed by peaks at m/z 1291, 1367, 1443, 1519, and 1595 could correspond to the chain with $(m+n)=16$, cationized with lithium, and/or to the chain with $(m+n)=13$, cationized with sodium, and/or to the chain with $(m+n)=10$, cationized with potassium.

A completely different behavior is observed in the case of TP3 terpolymer, containing only 15% of styrene. The m/z value of the peaks detected by MALDI-TOF-MS (*Fig. 11*) seems to be in accordance with the presence of a polymer chain *c* with a (trifluoroalkoxy)carbonyl moiety and an unsaturated fragment as end groups (*Fig. 12*). It is not possible, also in this case, to recognize if the unsaturated moiety derives from ethylene or from styrene. No polymer chain with a saturated end group is detected for this terpolymer. The m/z values seem to indicate a preferred cationization of the oligomers with sodium, even if it is not possible to exclude cationization also with lithium and potassium. For instance, the cluster formed by peaks at m/z 1229, 1305, 1381, 1457, and 1533 can be attributed to the chain with $(m+n)=15$, cationized with lithium,

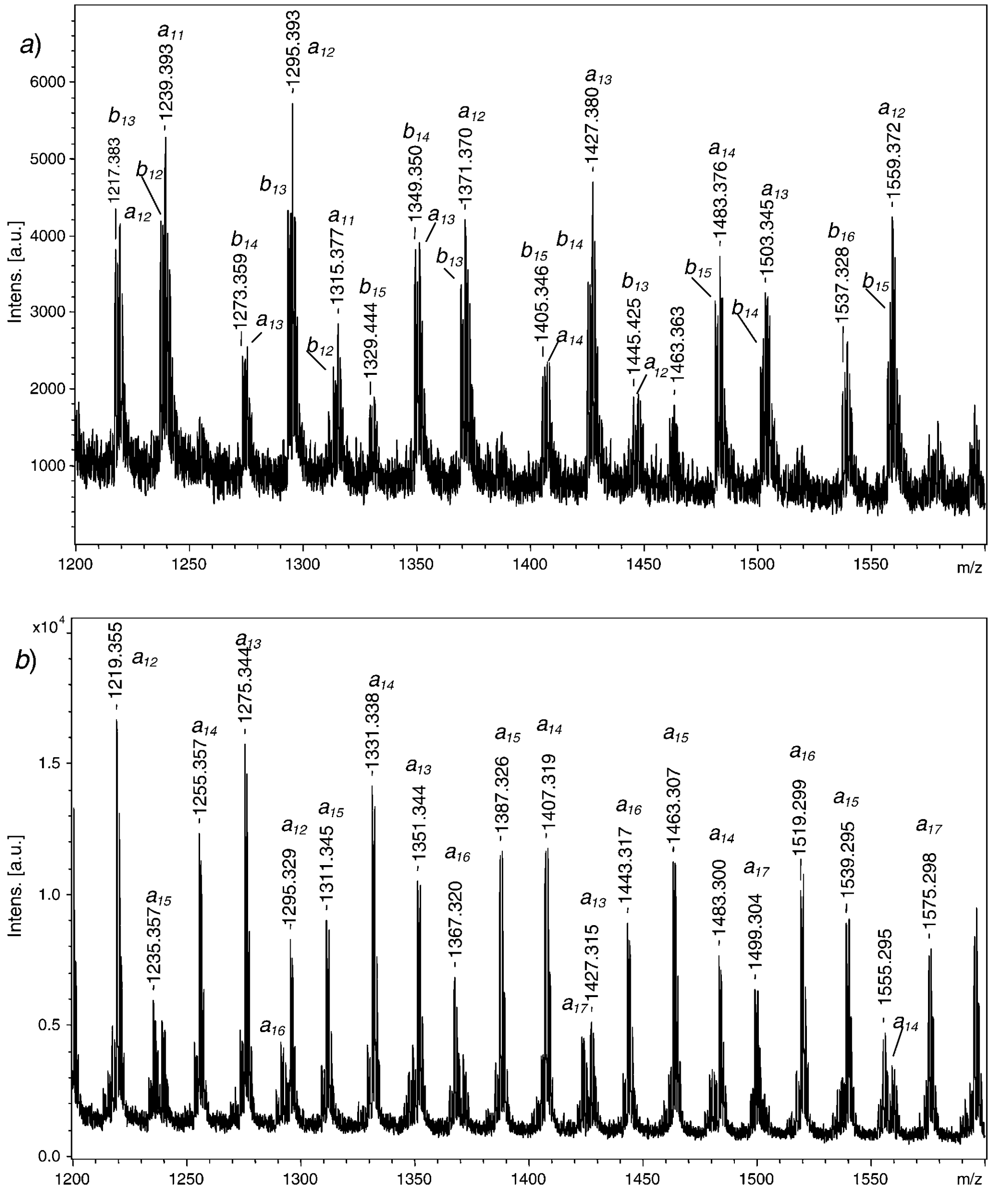


Fig. 10. *Enlarged view of the* m/z *1200–1660 region of the MALDI-TOF mass spectra of* Fig 9: a) *TP1* (77% styrene, 23% ethylene) *and* b) *TP2* (60% styrene, 40% ethylene). a_{m+n} and b_{m+n} refer to polymer *a* and polymer *b* cationized with lithium.

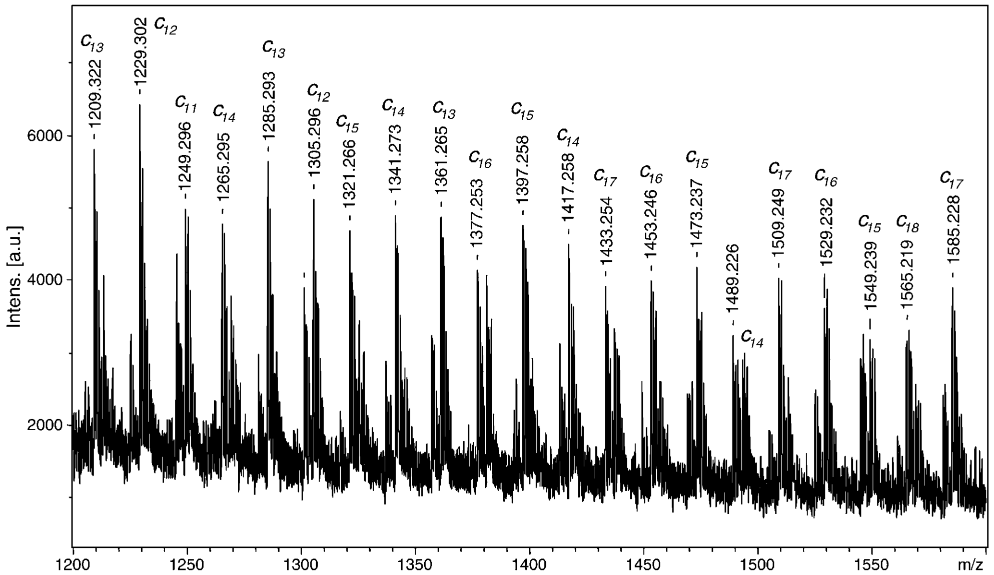
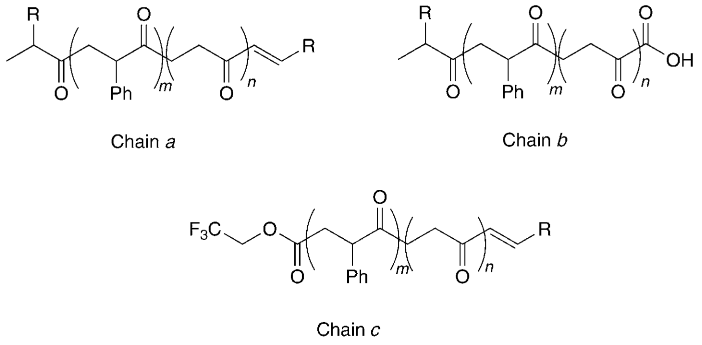


Fig. 11. *Enlarged view of the* m/z *1200–1660 region of the MALDI-TOF mass spectrum of* Fig. 9,c: *TP3* (15% styrene, 85% ethylene). c_{m+n} refers to polymer *c* cationized with sodium.



Chain *a*

Chain *b*

Chain *c*

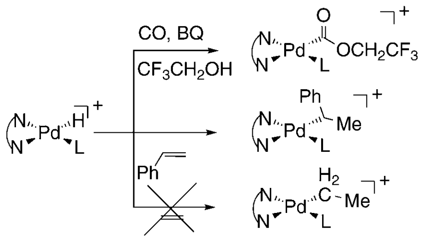
Fig. 12. *Polymer chains present in the CO/ethylene/styrene terpolymers* (R = H, Ph)

and/or to the chain with $(m+n)=12$, cationized with sodium, and/or to the chain with $(m+n)=9$, cationized with potassium.

It is straightforward to point out that, depending on the amount of styrene in the initial reaction mixture, different polymer chains are formed. In particular, no chains terminating with a (trifluoroalkoxy)carbonyl group were found in samples TP1 and TP2, obtained from reaction mixtures containing a higher initial amount of styrene than in the case of TP3, while in the latter sample, no chains with saturated end groups were present. While polyketones TP1 and TP2 were produced with a phen catalyst, terpolymer TP3 was synthesized by a bipy catalyst; however it seems to be very unlikely that the different end groups are related to the different catalyst since bipy and phen have always shown similar catalytic behavior.

These results represent an important issue for the knowledge of the mechanism of the terpolymerization reaction. On the basis of our previous data [12b], the (trifluoroalkoxy)carbonyl group originates from the reaction of benzoquinone with the [Pd(hydride)] species, reaction involving the solvent CF_3CH_2OH, followed by the insertion of CO into the Pd–OCH_2CF_3 bond. Thus, this reaction represents the initiation of a new polymer chain, and it is in competition with the initiation pathways based on the insertion of the alkene into the Pd–H bond (*Scheme 2*). The present results suggest that, when the concentration of styrene in the reaction mixture is low (5 ml), the reaction of the [Pd(hydride)] intermediate with benzoquinone is preferred with respect to the styrene insertion; the insertion of ethylene into the Pd−H bond is disfavored with respect to both the insertion of styrene and the reaction with benzoquinone; the saturated end groups of terpolymers TP1 and TP2 might exclusively originate from the insertion of styrene (and not of ethylene) into the Pd−H bond (*Scheme 2*).

Scheme 2. *Possible Steps Involving the [Pd(hydride)] Intermediate* (L = CO, styrene, ethylene, CF_3CH_2OH)



These mechanistic conclusions are in agreement with the catalytic data, in particular both with the effect of benzoquinone concentration and with the trend of CO uptake that indicated the oxidant as a necessary component of the catalytic system to achieve high productivities. In particular, at low concentration of the aromatic alkene, the oxidant is required to start a new catalytic cycle since the insertion of ethylene into the Pd−H bond seems to be unlikely.

Finally, as observed for the CO/styrene/*p*-methylstyrene terpolymers [6], even for the CO/ethylene/styrene terpolymers, the most abundant peak inside each cluster is shifted at lower m/z values on decreasing the initial amount of the alkene of higher molecular mass in the reaction mixture (*i.e.*, *p*-methylstyrene for the CO/styrene/*p*-methylstyrene terpolymers, or styrene for the CO/ethylene/styrene terpolymers). For instance, comparing samples TP1 and TP2, and considering only the polymer chain *a* cationized with lithium belonging to the cluster with $(m+n)=13$, the most abundant peak for the terpolymer containing 77% of styrene (TP1) is at m/z 1427, corresponding to $m=7$ and $n=6$, while for the terpolymer with 60% styrene (TP2), the most abundant peak is at m/z 1275, corresponding to $m=5$ and $n=8$. Therefore, these data confirm that the effect of the different amount of the two alkene monomers present in the polymer chain is clearly reflected in the MALDI-TOF mass spectra, as previously reported by us in the case of CO/styrene/*p*-methylstyrene terpolymers [6].

Conclusions. – In this paper, we showed that dicationic bis-chelated palladium(II) complexes containing a range of bidentate N-donor ligands, based on the 2,2′-bipyridine and 1,10-phenanthroline scaffolds, generate active catalysts for the CO/ethylene/styrene terpolymerization reaction. Both the catalytic activity and the relative content of the two alkenes in the polymer chain were modulated by the nature of the ligand. The highest productivity (16.4 kg TP/g Pd) was achieved with the [3-(*sec*-butyl)-1,10-phenanthroline]palladium complex [Pd(**10**)$_2$][PF$_6$]$_2$.

Comparing the present catalytic data with those previously reported by us in the corresponding CO/ethylene and CO/styrene copolymerization reactions promoted by the same precatalysts allows one to point out some important features of the catalytic system: *i*) the stability of the catalyst is remarkably affected by the different nature of the two alkenes; in particular, the aliphatic olefin has such a negative effect on the catalyst stability that neither the presence of the aromatic olefin nor the use of CF_3CH_2OH as reaction medium are able to prevent catalyst decomposition. *ii*) As a consequence, 1,4-benzoquinone is required to achieve high productivities, and the catalyst lifetime is dictated by the benzoquinone-to-palladium ratio. *iii*) MALDI-TOF-MS Analysis suggests that the insertion of ethylene into the Pd−H bond is unlikely, and, when the amount of styrene in the reaction mixture is low, the preferential initiation step involves the oxidant. This result represents an important difference with respect to the CO/aliphatic olefin copolymerization promoted by palladium complexes with diphosphine ligands, where ethylene insertion does take place as demonstrated by the presence of ethyl end groups in the polyketone chains [17]. *iv*) The lack of the effect of the 3-R-phen ligand on the molecular-mass values suggests that the aliphatic alkene could play the major role in the determination of the length of the polymer chains.

In conclusion, this study stresses once again the importance of the relationship, discovered by *Consiglio* in 1991 [4], between the nature of the ligand present in the catalyst and the nature of the alkene to be co- or terpolymerized. It provides as well some rational background for explaining which way the interplay of the two alkenes may address the mechanism of catalytic terpolymerization.

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Experimental Part

General. 2,2,2-Trifluoroethanol and styrene (*Aldrich*) for the catalytic reactions were used as received without any further purification. [Pd(OAc)$_2$] was a gift of *Engelhard Italia*. The ligands 2,2′-bipyridine (**1**), 4,4′-dimethyl-2,2′-bipyridine (**2**), 1,10-phenanthroline (**3**), 4,7-dimethyl-1,10-phenanthroline (**4**), and 3,4,7,8-tetramethyl-1,10-phenanthroline (**5**) are commercially available and were used as received. The 3-R-substituted 1,10-phenanthrolines **6**–**10** [18] as well as catalyst precursors [Pd(N−N)$_2$][PF$_6$]$_2$ (N−N = **1**–**10**) [11] were prepared as previously reported. ^{1}H- and ^{13}C-NMR Spectra: at 400 and 100.5 MHz, resp., with a *Jeol-EX-400* spectrometer; the resonances were referenced to the solvent peak *vs.* SiMe$_4$ (CDCl$_3$ at δ(H) 7.26 and δ(C) 77.0).

Terpolymerization Reactions. Polymerization reactions were carried out in a 150-ml stainless-steel autoclave equipped with a *Teflon* liner, a magnetic stirrer, a heating mantle, and a temperature controller.

The catalyst precursor $[Pd(N{-}N)_2][PF_6]_2$, 1,4-benzoquinone (BQ; when used), styrene, and the solvent CF_3CH_2OH were introduced in the autoclave, which was then pressurized with a 1:1 mixture CO/ethylene and heated to the desired temp. At the end of the catalysis and after cooling and releasing the residual gas, the soln. from the autoclave was poured into 200 ml of MeOH and stirred for one night causing the precipitation of the polymer, which was then isolated by decantation, washed with MeOH, and dried under vacuum.

The polymerization reactions reported in *Table 5* were carried out in a 300-ml stainless-steel autoclave equipped with a *Teflon* liner, a mechanical stirrer, a heating mantle, and a temp. controller, following the same procedure as reported above. ^{1}H-NMR ($CDCl_3$, r.t.): 7.35–7.10 (br., 5 arom. H); 4.1 (br., $PhCHCH_2$); 3.2 (br., 1 H, $PhCHCH_2$); 2.5 (br., 5 H, $PhCHCH_2$ and CH_2CH_2).

CO-Uptake Measurements. The polymerization reactions reported in *Fig. 6* were carried out in a 250-ml stainless-steel autoclave connected to a *Büchi-bpc* system to keep constant the CO/ethylene pressure and to monitor the CO uptake.

Molecular-Mass Measurements of Terpolymers. The molecular masses (M_w) of terpolymers and the molecular-mass distributions (M_w/M_n) were determined by gel-permeation chromatography (GPC) *vs.* polystyrene standards. The analyses were recorded on a *Knauer* HPLC (*K-501* pump, *K-2501* UV detector) with a *PLgel* (5 μm, 10^4 Å) GPC column and $CHCl_3$ as solvent (flow rate 0.6 ml/min). Samples were prepared as follows: 2 mg of the terpolymer were dissolved in 120 μl of 1,1,1,3,3,3-hexafluoropropan-2-ol (HFIP), and $CHCl_3$ was added up to 10 ml. The statistical calculations were performed with the *Bruker Chromstar* software.

MALDI-TOF-MS Measurements. Measurements were performed with an *Ultraflex-II* instrument (*Bruker Daltonik*, Bremen, Germany), operating in reflectron positive-ion mode. The instrumental conditions were: *IS1* = 25 kV; *IS2* = 21.65 kV; reflectron potential 26.3 kV; delay time 0 nsec. As matrix, 2-[(4-hydroxyphenyl)azo]benzoic acid (HABA) was used (sat. soln. in $CHCl_3$). Terpolymer (10 mg) was dissolved in HFIP (1 ml), and 5 μl of this soln. was added to the same volume of the matrix soln. About 1 μl of the resulting soln. was deposited on the stainless-steel sample holder and allowed to dry before introduction into the mass spectrometer. Three independent measurements were done for each sample. External mass calibration was performed with peptide calibration standard, based on the monoisotopic values of $[M+H]^+$ of angiotensin I, angiotensin II, substance P, bombesin, ACTH clip (1–17), ACTH clip (18–39), and somatostatin 28 at *m/z* 1046.5420, 1296.6853, 1347.7361, 1619.8230, 2093.0868, 2465.1990, and 3147.4714, resp.

REFERENCES

[1] T. Fujita, K. Nakano, M. Yamashita, K. Nozaki, *J. Am. Chem. Soc.* **2006**, *128*, 1968; A. Leone, G. Consiglio, *Helv. Chim. Acta* **2005**, *88*, 210; J. Kato, T. Taniguchi, Patent N° JP2005105470, 2005; T. Morita, S. Okada, Patent N° JP2005105471, 2005; M. Schmid, B. Rieger, U. Meier, Patent N° WO2004067603, 2004; G. Consiglio, in 'Late Transition Metal Polymerization Catalysis', Eds. B. Rieger, L. Saunders Baugh, S. Kacker, and S. Striegler, Wiley-VCH, Weinheim, 2003, p. 279.

[2] T.-W. Lai, A. Sen, *Organometallics* **1984**, *3*, 866; E. Drent, P. H. M. Budzelaar, *Chem. Rev.* **1996**, *96*, 663; A. Sommazzi, F. Garbassi, *Prog. Polym. Sci.* **1997**, *22*, 1547; B. Milani, G. Mestroni, *Comments Inorg. Chem.* **1999**, *20*, 301; C. Bianchini, A. Meli, *Coord. Chem. Rev.* **2002**, *225*, 35; W. P. Mul, A. W. van der Made, A. A. Smaardijk, E. Drent, in 'Catalytic Synthesis of Alkene–Carbon Monoxide Copolymers and Cooligomers', Ed. A. Sen, Kluwer Academic, 2003, p. 87; G. P. Belov, E. V. Novikova, *Russ. Chem. Rev.* **2004**, *73*, 267; J. Durand, B. Milani, *Coord. Chem. Rev.* **2006**, *250*, 542.

[3] K. Nozaki, N. Sato, H. Takaya, *J. Am. Chem. Soc.* **1995**, *117*, 9911.

[4] M. Barsacchi, G. Consiglio, L. Medici, G. Petrucci, U. W. Suter, *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 989.

[5] S. Kacker, A. Sen, *J. Am. Chem. Soc.* **1997**, *119*, 10028; B. Sesto, S. Bronco, E. L. Gindro, G. Consiglio, *Macromol. Chem. Phys.* **2001**, *202*, 2059; W. P. Mul, H. Dirkzwager, A. A. Broekhuis, H. J. Heeres, A. J. Van der Linden, A. G. Orpen, *Inorg. Chim. Acta* **2002**, *327*, 147.

[6] B. Milani, A. Scarel, J. Durand, G. Mestroni, R. Seraglia, C. Carfagna, B. Binotti, *Macromolecules* **2003**, *36*, 6295.

[7] a) A. Sen, Z. Jiang, *Macromolecules* **1993**, *26*, 911; b) M. Brookhart, F. C. Rix, J. M. DeSimone, *J. Am. Chem. Soc.* **1992**, *114*, 5894; c) M. Brookhart, M. I. Wagner, G. G. A. Balavoine, H. A. Haddou, *J. Am. Chem. Soc.* **1994**, *116*, 3641; d) A. Aeby, A. Gsponer, M. Sperrle, G. Consiglio, *J. Organomet. Chem.* **2000**, *603*, 122; e) B. T. Muellers, J.-W. Park, M. S. Brookhart, M. M. Green, *Macromolecules* **1999**, *34*, 572; f) A. Bastero, A. Ruiz, C. Claver, A. Bella, B. Milani, B. Moreno-Lara, F. A. Jalón, B. R. Manzano, *Adv. Synth. Catal.* **2005**, *347*, 839.

[8] a) A. Aeby, G. Consiglio, *Helv. Chim. Acta* **1998**, *81*, 35; b) A. Aeby, G. Consiglio, *J. Chem. Soc., Dalton Trans.* **1999**, 655.

[9] K. Nozaki, Y. Kawashima, K. Nakamoto, T. Hiyama, *Macromolecules* **1999**, *32*, 5168; Y. Kawashima, K. Nozaki, T. Hiyama, *Inorg. Chim. Acta* **2003**, *350*, 577.

[10] S. Kacker, J. A. Sissano, D. N. Schulz, *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 752; M. Auer, M. Kettunen, A. S. Abu-Surrah, M. Leskelä, C.-E Wilén, *Polym. Int.* **2004**, *53*, 2015.

[11] A. Scarel, B. Milani, E. Zangrando, M. Stener, S. Furlan, G. Fronzoni, G. Mestroni, S. Gladiali, C. Carfagna, L. Mosca, *Organometallics* **2004**, *23*, 5593.

[12] a) B. Milani, A. Anzilutti, L. Vicentini, A. Sessanta o Santi, E. Zangrando, S. Geremia, G. Mestroni, *Organometallics* **1997**, *16*, 5064; b) B. Milani, G. Corso, G. Mestroni, C. Carfagna, M. Formica, R. Seraglia, *Organometallics* **2000**, *19*, 3435; c) A. Scarel, J. Durand, D. Franchi, E. Zangrando, G. Mestroni, B. Milani, S. Gladiali, C. Carfagna, B. Binotti, S. Bronco, T. Gragnoli, *J. Organomet. Chem.* **2005**, *690*, 2106.

[13] B. Milani, E. Alessio, G. Mestroni, A. Sommazzi, F. Garbassi, E. Zangrando, N. Bresciani-Pahor, L. Randaccio, *J. Chem. Soc., Dalton Trans.* **1994**, 1903; B. Milani, L. Vicentini, A. Sommazzi, F. Garbassi, E. Chiarparin, E. Zangrando, G. Mestroni, *J. Chem. Soc., Dalton Trans.* **1996**, 3139; R. Santi, A. M. Romano, R. Garrone, L. Abbondanza, M. Scalabrini, G. Bacchilega, *Macromol. Chem. Phys.* **1999**, *200*, 25.

[14] J. Durand, E. Zangrando, M. Stener, G. Fronzoni, C. Carfagna, B. Binotti, P. C. J. Kamer, C. Müller, M. Caporali, P. W. N. M van Leeuwen, D. Vogt, B. Milani, *Chem.–Eur. J.* **2006**, published on the web June 28; DOI: 10.1002/chem..200501047.

[15] A. Gsponer, T. M. Schmid, G. Consiglio, *Helv. Chim. Acta* **2001**, *84*, 2986.

[16] A. Scarel, J. Durand, D. Franchi, E. Zangrando, G. Mestroni, C. Carfagna, L. Mosca, R. Seraglia, G. Consiglio, B. Milani, *Chem.–Eur. J.* **2005**, *11*, 6014.

[17] E. Drent, J. A. M. van Broekhoven, M. J. Doyle, *J. Organomet. Chem.* **1991**, *417*, 235.

[18] S. Gladiali, G. Chelucci, M. S. Mudadu, M. A. Gastaut, R. P. Thummel, *J. Org. Chem.* **2001**, *66*, 400.

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