# MALDI−TOF Mass Spectrometry in the Study of CO/Aromatic Olefins Terpolymers

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Over the past decade there has been an increasing interest in the development of new catalysts for polymerization[1] as well as of the techniques applied for the polymers characterization.[2] In particular, matrix-assisted laser desorption/ionization (MALDI) mass spectrometry is considered one of the most powerful analytical technique applied to polymers characterization.[2,3] Most of work done in this field is related to homopolymers, so relatively little has been reported on copolymers, and to the best of our knowledge, only one example of application of MALDI to terpolymers analysis has appeared.[4]

As far as new polymers are concerned, during the past few years much attention has been addressed to CO/olefin polyketones.[5] One of them, the CO/ethylene/propylene terpolymer, has been exploited at a commercial level by Shell under the name of Carilon. Nevertheless, little attention has been devoted to this class of polyketones, if compared to the corresponding copolymers. Moreover, the studies reported in the literature are related to CO/ethylene/styrene polyketones;[6] no mention is made on terpolymers of carbon monoxide with two aromatic olefins.

We reported that the catalytic system based on bischelated dicationic palladium complexes, $[Pd(N-N)_2][PF_6]_2$ (N−N = 1,10-phenanthroline and its substituted derivatives), efficiently promotes the CO/aromatic olefin copolymerization giving the corresponding polyketones in high yield (10.3 kg of CP/g of Pd; kg of CP/g of Pd = kilograms of copolymer per gram of palladium) and with high values of molecular weight ($M_w$ = 300 000), when the reaction is carried out in 2,2,2-trifluoroethanol (TFE) and without adding any oxidant.[7] The MALDI−TOF analysis of the synthesized copolymers allowed the recognition of the end groups, evidencing that the $\beta$-hydrogen elimination is the only effective chain-end process.[7b] Now, we have extended our investigation to the CO/styrene/4-Me-styrene terpolymerization reaction (Scheme 1).

The terpolymerization tests were run in trifluoroethanol, at 50 °C, under 40 atm of CO pressure without the addition of any cocatalyst or coreagent. The synthesized polyketones were characterized by $^1$H and $^{13}$C NMR spectroscopy, by MALDI−TOF spectrometry, and by SEC.

**Scheme 1. Terpolymerization Reaction**

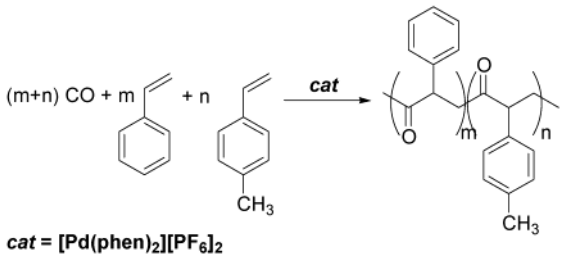


**Table 1. CO/Styrene/4-Methylstyrene Terpolymerization Showing the Effect of the Relative Amount of the Two Olefins with Catalyst Precursor $[Pd(phen)_2][PF_6]_2$[a]**

| styrene/ 4-Me-styrene (v/v) | g of TP | kg of TP/g of Pd | $M_w$ ($\langle M_w\rangle/\langle M_n\rangle$) | % styrene[b] |
|---|---|---|---|---|
| 1/0 | 0.86[c] | 1.50 | 108 000 (1.9) | 100 |
| 0/1 | 2.28[c] | 4.00 | 130 000 (1.9) | 0 |
| 1/1 | 1.43 | 2.50 | 125 000 (2.6) | 42 |
| 2/1 | 1.19 | 2.07 | 130 000 (2.5) | 58 |
| 5/1 | 0.98 | 1.71 | 101 000 (2.3) | 70 |
| 10/1 | 0.91 | 1.58 | 110 000 (3.0) | 80 |

[a] Reaction conditions: $n_{Pd} = 0.54 \times 10^{-5}$ mol; $P_{CO}$ = 40 atm; $T$ = 50 °C; solvent TFE, $V$ = 20 mL; $t$ = 24 h; styrene + 4-Me-styrene, $V$ = 30 mL. [b] Amount of styrene in the polymeric chain, determined on the basis of the $^{13}$C NMR spectra. [c] The solids are CO/styrene and CO/4-Me-styrene copolymers.

The productivity of the system falls between the typical values of the two corresponding copolymerization reactions, CO/styrene and CO/4-Me-styrene, regardless of the ratio of the two olefins present in the reaction mixture (Table 1). A decrease of productivity and molecular weight is found on increasing the initial amount of styrene with respect to 4-Me-styrene (Table 1). These data are in agreement with our previous results indicating that 4-Me-styrene is more reactive than styrene.[7c] Nevertheless, for all the terpolymerizations studied productivities higher than 1 kg of TP/g of Pd are reached and the molecular weight values of the synthesized polyketones are between 100 000 and 130 000.

It should be noted that in all cases no formation of palladium black is observed, confirming the stability of the active species under the reaction conditions used.

The first evidence that the reaction products are terpolymers and not a mixture of the corresponding copolymers derives from the complete solubility of the solid in chloroform in contrast to the insolubility of the CO/styrene polyketone in the same solvent. Therefore, the NMR characterization was performed by recording the spectra in $CDCl_3$. In the $^1$H NMR spectra both the methinic and methylenic protons give only one broad signal (centered at 4.07 ppm and at 3.04 and 2.61 ppm, respectively), regardless if they belong to styrene or 4-Me-styrene. Instead, in the $^{13}$C NMR spectra the methinic carbon of the two olefins generates two different signals depending on the olefin present in the repetitive unit. The intensity of these signals varies by changing the ratio of the two olefins in the reaction mixture (Figure 1).

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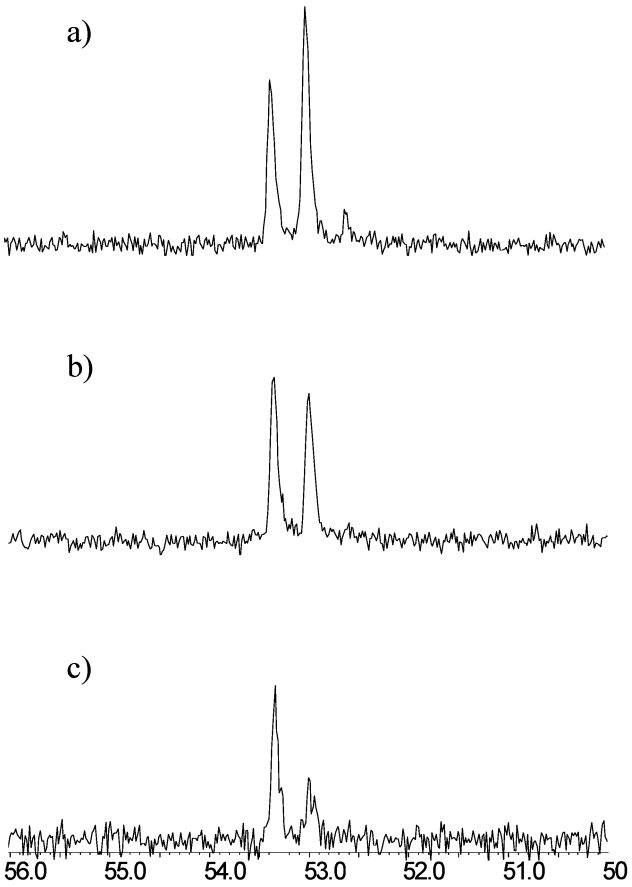


**Figure 1.** $^{13}C$ NMR spectra of CO/styrene/4-Me-styrene terpolymers in $CDCl_3$ (*CH* region). Variations observed with the styrene/4-Me-styrene ratio: (a) 1/1; (b) 2/1; (c) 5/1.

The signal at 53.30 ppm is attributed to the CO/styrene repetitive unit, while that at 53.00 ppm is related to the CO/4-Me-styrene unit. From the integration of these signals the relative amount of the two olefins inserted in the polymeric chain is calculated, and values ranging from 40% to 80% of content of styrene are found (Table 1).

**Table 2. CO/Styrene/4-Methylstyrene Terpolymers Showing Analysis of a Peak Inside the Cluster with $m + n = 6$ of the MALDI−TOF Spectrum of the Sample 2/1[a]**

| assign $m + n$ | $+Li^+$ | $+Na^+$ | $+K^+$ |
|---|---|---|---|
| 6 + 0 | | | 803.60 |
| 5 + 1 | | 801.60 | 817.66 |
| 4 + 2 | 799.60 | 815.66 | 831.39 |
| 3 + 3 | 813.66 | 829.39 | 845.49 |
| 2 + 4 | 827.39 | 843.49 | 859.38 |
| 1 + 5 | 841.49 | 857.48 | 873.48 |
| 0 + 6 | 855.48 | 871.38 | |

[a] The experimental values of *m*/*z* are reported in the columns; *m* is the number of repetitive units containing styrene, *n* is the number of repetitive units containing 4-Me-styrene.

As in the case of copolymers,[7b] the MALDI−TOF data on the molecular weight distribution are different from those obtained by SEC analysis due to the relatively high polydispersity of these terpolymers. However, the terpolymer structure is clearly pointed out by the MALDI−TOF analysis carried out in low molecular weight region (600−2000 *m*/*z*). These MALDI spectra consist of very well-defined clusters, each due to polymeric chains formed by the same number of repetitive units, i.e., $(m + n)$ value (Scheme 1). Each oligomeric chain is detected as a cationized species (adduct with lithium, sodium, and potassium), even if no cationization agent was added to the terpolymer analyzed solution (Table 2).

The high mass resolution of the instrument allows the identification within each cluster, with the same $(m + n)$ value, of polymeric chains constituted of different number of styrene (*m* value) and 4-Me-styrene (*n* value) residues (Figure 2).

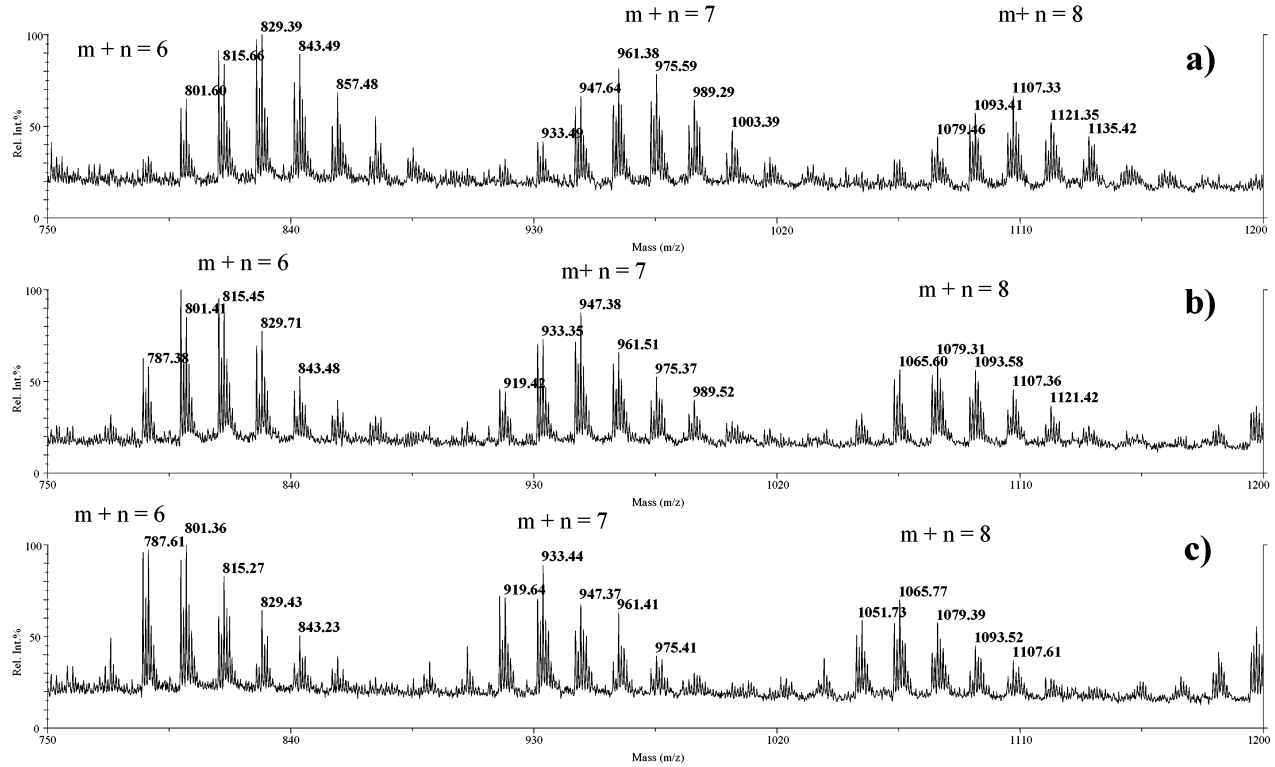


**Figure 2.** MALDI−TOF mass spectra of CO/styrene/4-Me-styrene terpolymers. Variations observed with the styrene/4-Me-styrene ratio: (a) 2/1; (b) 5/1; (c) 10/1. An enlarged region.

The comparison of the MALDI−TOF mass spectra of the three terpolymers, differentiating for the relative amount of the two olefins inserted, evidences that, within each cluster, the relative abundance of the oligomer containing more styrene residues increases on increasing the initial styrene amount in the reaction mixture. For instance, considering only the sodium cationized oligomers in the cluster with $m + n = 7$, for the terpolymer containing 58% of styrene the most abundant peak is at $m/z$ 961.38, corresponding to $m = 4$ and $n = 3$; for the terpolymer with 70% of styrene the most abundant peak is at $m/z$ 947.38, corresponding to $m = 5$ and $n = 2$; and, finally, for the terpolymer with the 80% of styrene, the most abundant peak is at $m/z$ 933.44, corresponding to $m = 6$ and $n = 1$ (Figure 2).

Therefore, thanks to the MALDI analysis it is possible to confirm the terpolymeric nature of the synthesized polyketones, and in contrast to a previous paper about terpolymers,[4] in this case there is a one-to-one correspondence between the peak and assignment. Contrary to what was obtained by MALDI analysis of copolymers,[7b] the unequivocal determination of the nature of the end group present in a single oligomeric chain is, in this case, impossible. In fact, the unsatured and satured end groups can originate from both styrene and 4-Me-styrene moieties, and this feature leads to the formation of isobaric ions, impossible to distinguish.

In conclusion, with the catalytic system reported above, the CO/styrene/4-Me-styrene terpolymers are here synthesized for the first time in high yield (up to 2.50 kg of TP/g of Pd) and with high molecular weight (up to 130 000). For the second time MALDI−TOF analysis is applied to the study of a terpolymer by allowing the unambiguous determination of chemical composition of the macromolecules, and for the first time, the effect of the different amounts of the two olefin monomers present in the polymeric chain is clearly evidenced in the MALDI mass spectra. An analogous investigation is carrying out on CO/ethylene/styrene terpolymers.

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**Supporting Information Available:** Text giving the Experimental Section and figures showing the $^{13}C$ NMR spectrum and MALDI−TOF mass spectra, full region. This material is available free of charge via the Internet at http://pubs.acs.org.

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