

# Use of mass spectrometry for the analysis of molecular weight distribution and macrocycles in functionalized oligo- $\epsilon$ -caprolactones synthesized by heterogeneous AROP in protic conditions

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## Summary.

Functionalized oligo- $\epsilon$ -caprolactones synthesized by heterogeneous coordinated anionic ring opening polymerization (AROP) in protic conditions have been analyzed by mass spectrometry in order to investigate the molecular weight distribution as well as the possible occurrence of macrocycles.

Mass spectra obtained from LSIMS revealed the presence of fragmentation products and some of them have been identified. Macrocycles were also detected. Nevertheless, ESI and MALDI-TOF spectrometries do not confirm the presence of macrocycles in the samples. The same results have been obtained by analysis of commercially available polycaprolactones.

## Introduction.

A few years ago, we presented a new heterogeneous catalytic system able to open oxygenated rings such as oxiranes and lactones in protic conditions (1). The active centers are aluminium alkoxides grafted on a solid porous support such as silica. The addition of alcohol molecules induces transfer reactions between the grafted alkoxides and the free alcohols so that there are more polymer chains produced than there are metal atoms (Figure 1). The innovative aspects of this process are firstly the various functionalities brought by the starting alcohol and secondly, the possibility of recycling the active centers and developing a continuous polymerization process (2). The great versatility of this method for the synthesis of functionalized oligomers has been reported (3,4).

Dealing with a new catalytic system, the characterization of these oligomers is quite of importance because the chemical structure can be in a way seen as the signature of the catalytic system. In this case, the question was to see what changes could be brought by this system with respect to a conventional initiator for coordinated AROP, namely the grafting of the active centers on a solid support and the addition of alcohol molecules.

This paper reports some results obtained in the analysis of some functionalized oligo- $\epsilon$ -caprolactones ( $\epsilon$ -CL) by mass spectrometry techniques such as LSIMS, electrospray-MS and MALDI-TOF MS. Some commercially available polycaprolactones have also been analyzed by the same techniques in order to valid our conclusions.

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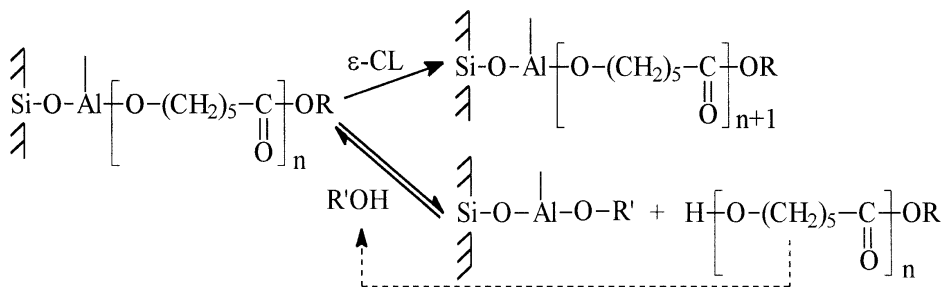


Figure 1. Propagation vs. transfer reaction in the AROP in protic conditions. The dotted arrow depicts the ability for the functionalized oligomers to act as a transfer agent.

## Experimental.

The synthesis of functionalized oligo- $\epsilon$ -caprolactones and their characterization by NMR have been reported in previous publications (3,4). Liquid secondary ion mass spectrometry (LSI MS) analysis were performed on a ZAB2SEQ (Micromass) using a caesium gun. The matrices used were *m*-nitrobenzyl alcohol (NBA) and NBA mixed with NaCl or LiCl. The positive electrospray spectra were obtained from  $\text{CHCl}_3/\text{MeOH}$  solutions with NaI in FIA mode on a VG-platform single-quadrupole mass spectrometer Micromass. The MALDI-TOF data were obtained with a Micromass TOF Spec-E mass spectrometer operating in reflectron mode. Ions generated in the source region by means of a  $\text{N}_2$  laser (337 nm) were subjected to a 25 kV potential and detected by a dual microchannel plate (MCP) detector. The matrix used was 2,5 dihydroxybenzoic acid (DHB) doped with sodium ions to increase the magnitude of the polymer signal.

## Results and discussion.

### *General features of the homogeneous AROP in protic conditions.*

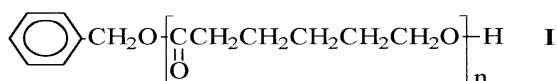
Some papers have already presented the general features of this polymerization system in homogeneous medium with  $\text{Al}(\text{OiPr})_3$  as initiator and various alcohols as transfer agents (1,3,<sup>5</sup>). The determination of the molecular weight distribution (MWD) as well as its dependence on the conversion have been fully investigated. It was observed that the average degree of polymerization can be controlled by the  $[\text{Monomer}]/[\text{Alcohol}]$  ratio and increases with conversion. Furthermore, the MWD is narrow, and the polydispersity index decreases as the molecular weight increases (4).

It is known that AROP of  $\epsilon$ -CL may lead to backbiting reactions when using stanous-based initiators. Those based on aluminium and alkylaluminium alkoxides generally give rise to living polymerizations without generation of side products(6,7). In our case, the free alcohol molecules can coordinate the Lewis acid as an additional ligand which would increase the nucleophilicity of the oxygen atom of the aluminium alkoxide. The effect on the possible formation of macrocycles is not known. These macrocycles cannot be detected by NMR since they do not induce neither additional resonance peaks nor variation of the related intensities, so that the determination of the degree of polymerization by NMR would lead to a false value. Nevertheless, they would alter the molecular weight distribution, particularly in case of a high relative abundance and low molecular weight compounds would have been detected by GPC investigations, that is not the case (4).

Due to these features, this system can be classified as a living system with reversible transfer (8). In addition, the narrow MWD means the transfer frequency is fast enough with respect to the propagation steps.

*The problem of the determination of the MWD in heterogeneous conditions.*

In heterogeneous systems,  $^1\text{H}$  NMR investigations have clearly shown that the number-average molecular weight was also controlled by the Monomer/[Alcohol] ratio and increased with conversion (1,3). The oligo- $\epsilon$ -caprolactones used in this study were synthesized by using benzyl alcohol as transfer agent because the benzyl moiety is a convenient group to label the chain ends ( $\alpha$ -benzyl  $\omega$ -hydroxy polycaprolactone I).



Nevertheless, some drawbacks in the analysis come from the silica itself : the porous structure is issued from the aggregation of elementary silica nodules and the polymerization process may cause the desaggregation of a few nodules which act as physical crosslinks. It is very difficult to get rid of these particles because the polymer chains may complex them. The hydrodynamic radius of the polymer chains is then highly increased so that the GPC results become questionable. The determination of the actual MWD remains to be done, although the amount of residual free alcohol in the case of very low degrees of polymerization has been correlated with a Poisson distribution (5).

*Mass spectrometry of  $\alpha$ -benzyl  $\omega$ -hydroxy polycaprolactone.*

Mass spectrometry appears to be a method of choice to overcome these difficulties, provided soft ionisation techniques are used in order not to break the polymer chains. The question is to be sure of the MWD as deduced from this technique. Some papers have reported the analysis of poly(ethylene glycols) and their derivatives by fast atom bombardment (FAB). The fragmentation of the  $(\text{M}-\text{Na})^+$  species derived from the highest oligomers cannot be avoided while the distribution of the protonated molecular ions  $(\text{M}-\text{H})^+$  is in a good agreement with that deduced by SEC (9, 10). It seems now that MALDI-TOF MS is the convenient method to analyze polymers without fragmentations (11).

Figure 2 displays the mass spectrum of an  $\alpha$ -benzyl  $\omega$ -hydroxy polycaprolactone obtained by LSIMS, a technique close to FAB-MS. It appears that the expected distribution is not observed at all: besides peaks detected at  $m/z = 108 + 114n + 1$  which are related to the functionalized oligocaprolactones  $(\text{M}-\text{H})^+$  appear other peaks at  $m/z = 114n + 1$ . These latter are related to  $[(\text{CL})_n-\text{H}]^+$ , which may be either linear or cyclic.

The macrocycles may be due to a transesterification occurring at the same time as the polymerization. The occurrence of this product would be a drawback for the further development of this synthesis method.

The other hypothesis is the fragmentation of the polymer chains because of the required ionization and vaporization of the sample during the mass spectrometry analysis. Some molecular ions may be produced, but fragments can also appear from too energetic particles or by collisions between the different species present in the source.

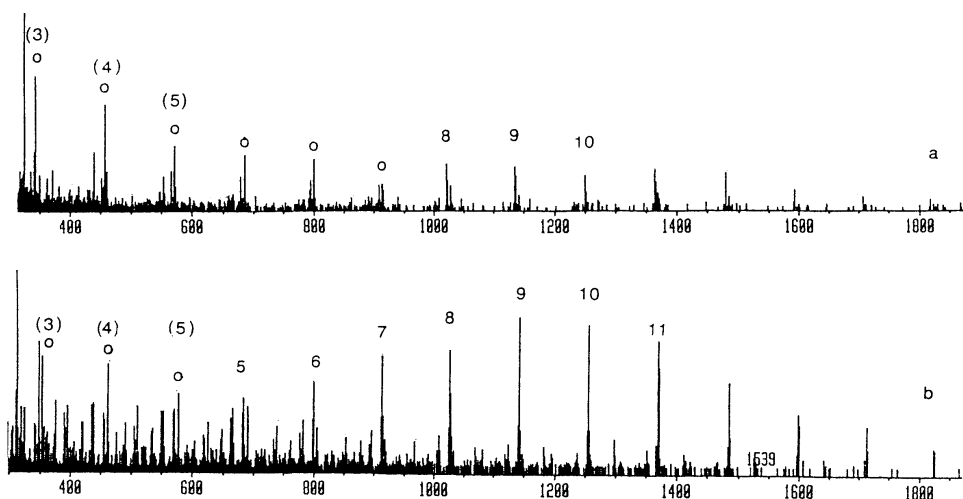


Figure 2. (a) LSIMS of a  $\alpha$ -benzyl  $\omega$ -hydroxy polycaprolactone with NBA as matrix. (b) effect of the addition of LiCl in the matrix. The circles denote the peaks detected at  $m/z = 114n + 1$ . The numbers indicate the degree of polymerization.

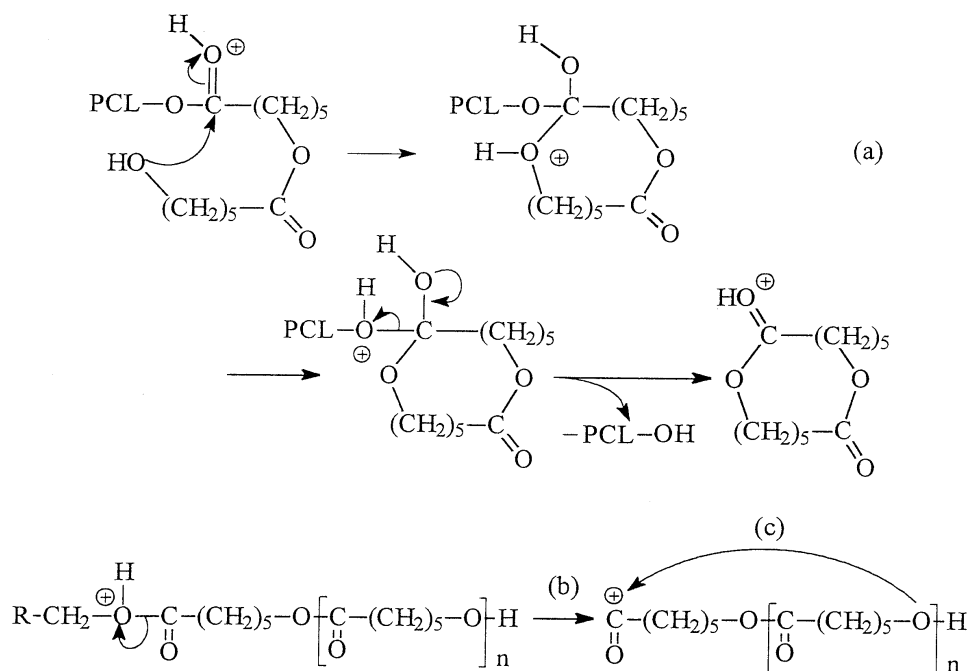


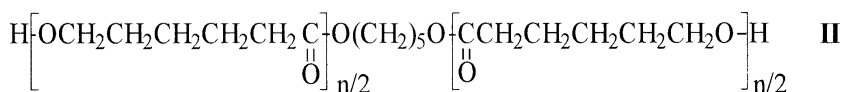
Figure 3. Formation of macrocycles by acid-catalyzed transesterification (a) and linear products (b) according to the location of the protonated oxygen atom in the polymer chain. Both fragmentations lead to compounds detected at  $m/z = 114n + 1$ . A subsequent cyclization can also occur according to (c) to give cyclics.

Macrocycles can be produced by acid-catalyzed transesterification following the protonation of the oxygen atom of the carbonyl group (Fig. 3a). The protonation of the other oxygen atom leads to another linear fragmentation product (Fig. 3b). This reaction is even more probable because the attack of the hydroxyl end-group is not required as in the formation of the macrocycle. As depicted in Fig. 3c, a subsequent cyclization can also occur to give cyclics. Since the general features of the polymerization in homogeneous medium display a quasi living character without formation of any macrocyclics, the above results suggest that the products related to the peaks detected at  $m/z = 114n + 1$  could be issued from the mass spectrometry analysis. In order to valid this hypothesis, we analyzed commercially available polycaprolactones. The same trends are observed for all the polyesters and the following paragraph reports the relevant features.

*Mass spectrometry of linear  $\alpha$ - $\omega$ -hydroxytelechelic polyesters.*

CAPA<sup>®</sup> (from Interlox Chemicals) are linear  $\alpha$ - $\omega$ -hydroxytelechelic polyesters used as chain extenders in polyurethanes synthesis. We present below the relevant features of the analysis of one of them, namely CAPA 210 (II).

A molecular weight can be deduced from its hydroxyl value, which is equal to 1000 g/mol. <sup>1</sup>H NMR allows to get the number average degree of polymerization  $n = 8$ , in a good agreement with the previous value. GPC results ( $M_n = 1040$ ; PDI = 1.43) are also in a good agreement (12). The fact that the PDI value is slightly higher than expected from a Poisson distribution agrees with the fact that polymerizations are performed with stannous-based catalysts, known to give backbiting reactions.



The LSIMS mass spectra of CAPA 210 is displayed on Figure 4a. The peaks observed at  $m/z = 114n + 104 + 1$  can be assigned to the protonated molecular oligomers with a central moiety issued from pentanediol. However, the intensity of the molecular species does not agree at all with the expected MWD. A lot of peaks appear at  $m/z = 114n + 1$ . Some dehydrated products  $(\text{MH} - \text{H}_2\text{O})^+$  can also be noticed at  $m/z = 114n + 87$ .

The appearance of mass spectrum changes in a noticeable way when carrying out the analysis in the presence of NaCl or LiCl (Figure 4b). Adding sodium or lithium salt causes the apparition of a distribution of the oligomers, the best result being obtained with LiCl ( $m/z = 114n + 104 + 7$ ). Nevertheless, the highest intensity appears as the molecular peak corresponding to  $\text{DP}_n = 4$ , for an expected value ( $\text{DP}_n = 7$ ). However, it must be underlined that the peak maximum does not necessarily correspond to the  $\text{DP}_n$ .

On the other hand, electrospray measurement, although being a softer technique, give results which remain rather questionable for the MWD determination (Fig. 5). It is clear that the amount of cyclics is highly reduced, which allows to conclude that backbiting reactions occur during the LSI MS analysis. However, a distribution of doubly charged ions  $(\text{M} + 2 \text{Na})^{2+}$  appears at  $m/z$  values which are half the actual values (this distribution is characterized by a mass increment of 57 from one peak to the next, equal to half the molecular weight of the  $\epsilon$ -CL unit), so that both  $\text{DP}_n$  and MWD cannot be accurately determined. In addition, it was shown that the distribution depends on the cone voltage.

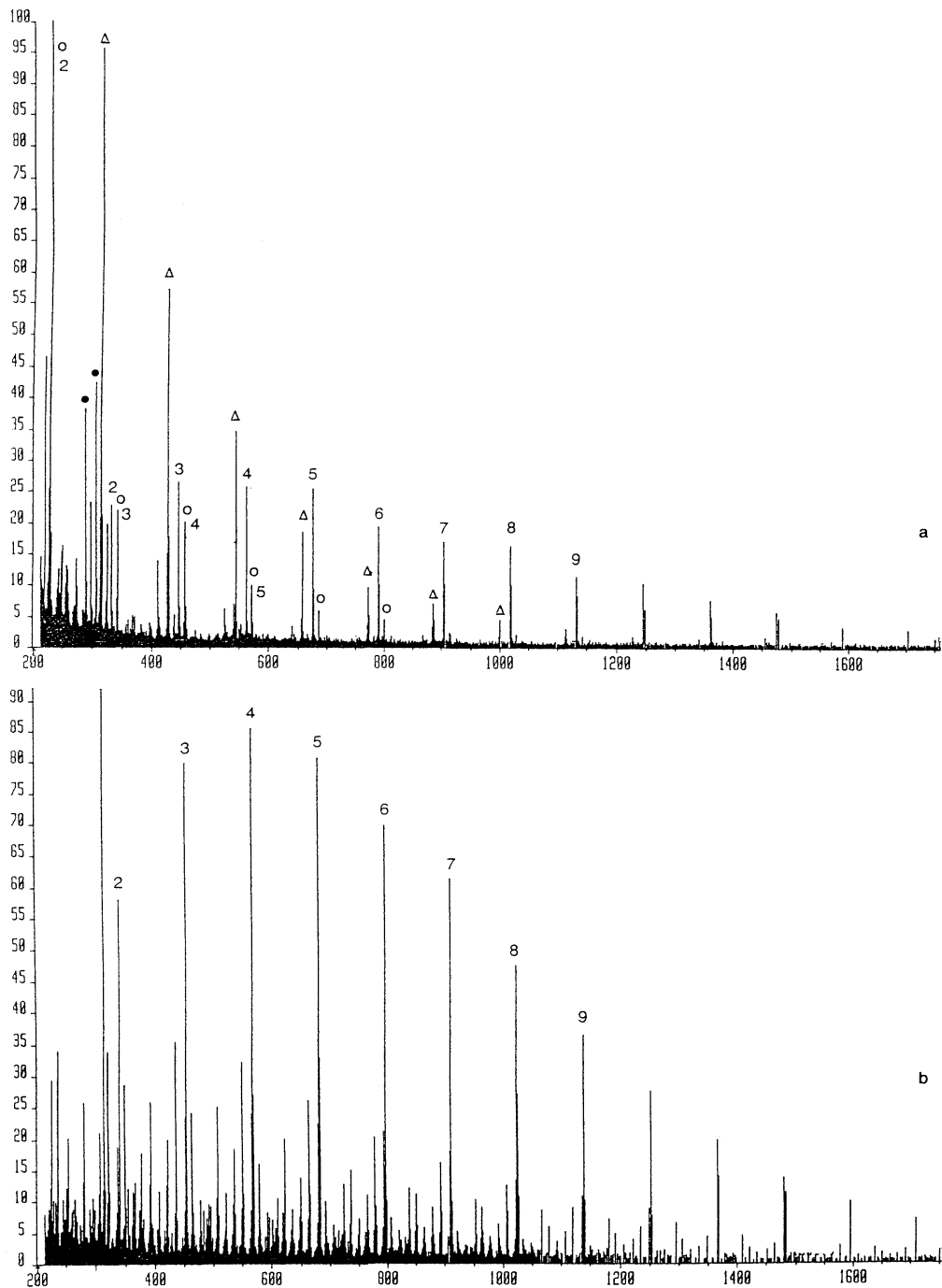


Figure 4. (a) Mass spectrum of CAPA 210 with NBA as matrix. The circles denote the peaks at  $m/z = 114n + 1$ . The numbers indicate the degree of polymerization. The dehydrated product is indicated by open triangles. The peaks at  $m/z = 289$  and  $307$  (black points) are due to the NBA ( $M = 153$ ):  $289 = [2MH - H_2O]^+$ ;  $307 = [2MH]^+$ . (b) Mass spectrum of CAPA 210 with NBA-LiCl matrix.

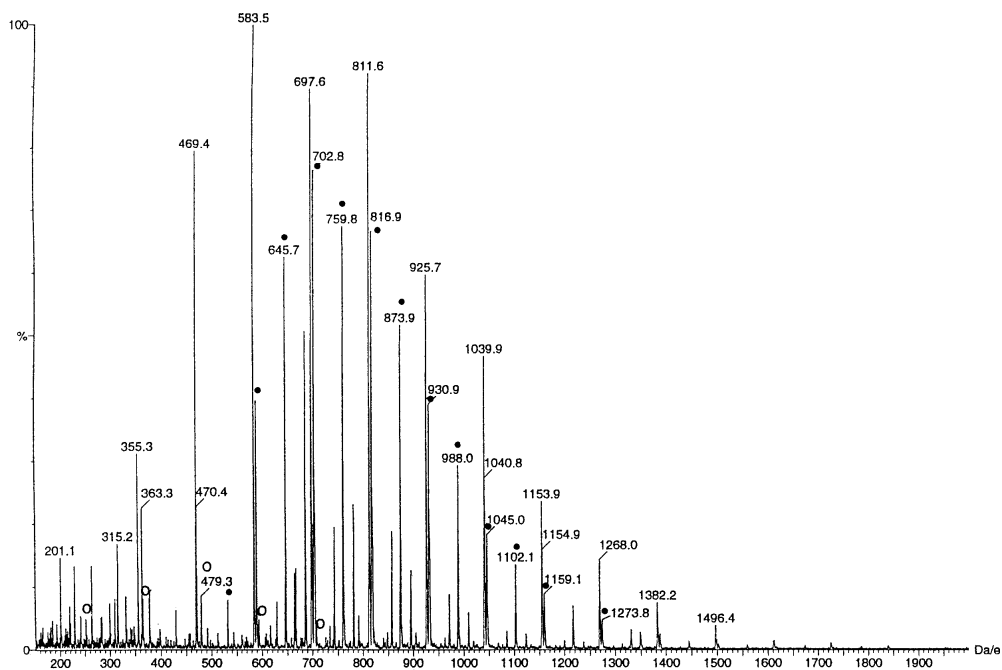


Figure 5. Electrospray mass spectrum of CAPA 210 (the salt is NaI). The open circles denote the peaks at  $m/z = 114n+1$ . The doubly charged ions are indicated by black points.

Finally, we used MALDI-TOF MS for the analysis of a  $\alpha$ -benzyl- $\omega$ -hydroxyoligo-caprolactone synthesized from a [Monomer]/[Alcohol] ratio = 10. The mass spectrum is displayed in Fig. 6. The highest intensity is observed for the molecular peak (M-Na)<sup>+</sup> at  $m/z$  1272.9 ( $n = 10$ ) and macrocycles are no longer observed. The MWD tends to spread towards high molecular weights with a PDI equal to 1.39. This may be due to the fact that the probability of the transfer reaction is decreasing as the chain length, and then the viscosity, increases. Another reason could be an ionization and desorption process depending on the molecular weight.

## Conclusion.

Functionalized oligo- $\epsilon$ -polycaprolactones have been synthesized by a new heterogeneous catalytic process in protic conditions so that the degree of polymerization can be controlled by the [Monomer]/[Alcohol] ratio. The products have been analyzed by using different mass spectrometry techniques (LSI, ESI and MALDI-TOF) in order to precise the chemical nature of the chain ends and to get an estimation of the NWD.

It was found that the values of the degree of polymerization is not in agreement with the <sup>1</sup>H NMR results as well as the [Monomer]/[Alcohol] ratio. Furthermore, the results depend on the techniques themselves. Analyses of available commercially  $\alpha$ - $\omega$ -hydroxy-telechelic polycaprolactones by the same methods display the same tendencies, that clearly shows these problems are due to the techniques and not to the polymerization process.

Mass spectrometry analyses by LSI MS display a first distribution of molecular peaks, assigned to the linear oligomers, with molecular weights lower than expected and a second one due to cyclics. The analyses performed by ESI and MALDI-TOF do not confirm the presence of these cyclics which are probably due to reactions taking place during the LSIMS analysis.

These results confirm the fact that ESI and MALDI-TOF spectrometries are softer methods than LSIMS for macromolecules analyses, without any fragmentation process. Nevertheless, the presence of doubly charged ions with ESI MS impedes an accurate determination of MWD. MALDI-TOF MS is a more convenient method, provided the polydispersity index remains narrow. Finally, the another important point for the polymer synthesis point of view is the great versatility of this heterogeneous catalytic system for getting well-defined functionalized oligo- $\epsilon$ -caprolactones without macrocycles.

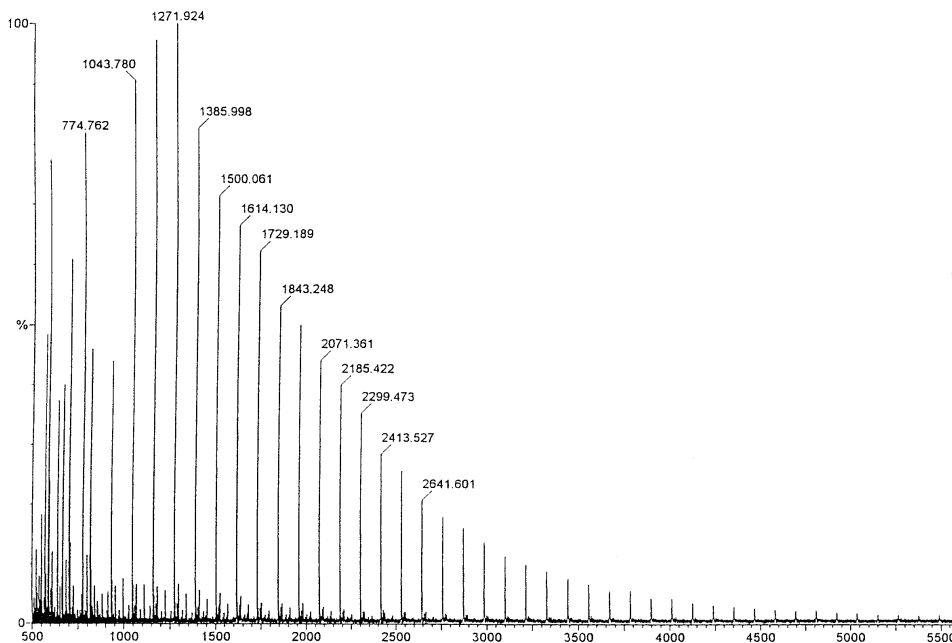


Figure 6. MALDI-TOF spectrum of a  $\alpha$ -benzyl  $\omega$ -hydroxy polycaprolactone (in 2,5 DHB + NaCl);  $m/z = 114n + 108 + 23$ .

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