

Bulk functional oligomerization of ϵ -caprolactone in a mini extruder

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Summary

ϵ -caprolactone has been polymerized in bulk in a mini-extruder with $\text{Al}(\text{O}i\text{Pr})_3$ as initiator and benzyl alcohol as transfer agent. Polymer chains have been characterized by ^1H NMR, SEC and Maldi-Tof mass spectroscopy in order to investigate the potentialities of this process in terms of macromolecular engineering. Low temperatures around 75°C are enough to perform oligomerization at high conversion with a mean residence time less than 2 minutes. All the polymer chains are actually functionalized by the chemical group issued from the transfer agent. Molecular weight distribution depends on the temperature as well as on the residence time.

Introduction

Ring opening polymerization of ϵ -caprolactone has widely been investigated because of the large number of applications, such as biocompatibility, biodegradability and miscibility with other polymers[1]. Aluminum isopropoxide and tin octoate are probably the most frequently encountered initiators, but some other metal salts are now reported in the literature, and among them, the rare earth alkoxides appear quite promising [2]. The polymerization is described according to the well-known coordination - insertion mechanism [3]. Depending on the initiator, side reactions such as transesterifications and backbiting can be avoided and a living character is sometimes observed.

Practically, polymerizations are nearly exclusively carried out in homogeneous processes by using a batch reactor according to a stoichiometric process : the number of polymer chains is restricted to the number of metal atoms or alkoxide ligands, depending on the initiation efficiency. It was later found that adding transfer agents such as alcohols is a versatile way to increase the number of macromolecules as well as to get functionalized oligomers [4].such as alcohols is a versatile way to increase

the number of macromolecules as well as to get functionalized oligomers [5].

An innovation was to graft the active centers onto a solid porous support : besides the synergy brought by the combination of the support and the active center itself (the solid support acts as an actual ligand of the active center and modifies its intrinsic reactivity [6]), it was possible to develop a new polymerization continuous process by using a plug flow reactor [7]. In that case, the transfer reaction is the key-step since it allows the polymer chains to move all along the reactor. Otherwise, the chains would stay grafted onto the active centers and could not be recovered at the output of the reactor. The chain length is directly connected to the reaction time, that is to the residence time inside the reactor.

Another interesting way to perform a continuous polymerization is to use an extruder as the reactor. Contrary to the above mentioned processes, a certain advantage in that case is to allow a bulk polymerization with a high reaction rate. In addition, there is no organic solvent to eliminate to recover the final product. Nevertheless, one of the main problems is the transposition of the reaction, previously carried out in solution at low temperatures, to the harder conditions usually encountered in the extruder. A first approach was reported by Feijen to get polylactide from L-lactide with $\text{Sn}(\text{Oct})_2$ as initiator at 180°C [8]. Increasing the amount of $\text{Sn}(\text{Oct})_2$ up to 1 % leads to the monomer conversion. The molecular weight distribution increases from 1.1 to 1.5. more recently, Cassagnau studied the polymerization of ϵ -caprolactone by using titanium tetrapropoxide as the initiator [9,10]. It was found that the molecular weight depends on the conversion but the molecular weight distribution is close to 2, rather far from the theoretical limit value $1 + 1/\bar{X}_n$. This discrepancy was attributed to the transesterification reactions induced by the initiator. In the aim of the macromolecular engineering, these side reactions may be an important drawback and it deserves to find how to limit or to get rid of them.

This paper deals with the polymerization of ϵ -caprolactone in a mini-extruder with aluminum isopropoxide as the initiator and benzyl alcohol as a transfer agent. The polymer chains were characterized by NMR, SEC chromatography and Maldi-Tof mass spectroscopy. In that preliminary study, the problem was not only to check the feasibility of the process (that is the polymerization when using alcohol as transfer agent in the extruder), but also to investigate the potentiality of macromolecular engineering in terms of functionality of the polymer chains, average number molecular weight as well as molecular weight distribution.

Experimental Part

ϵ -caprolactone and benzyl alcohol (Aldrich) were used as received and kept under molecular sieves 3Å. The polymerization was carried out at various temperatures in a screw extruder (type "Rheoscam" – Scamia; screw diameter : 20 mm, screw length : 230 mm).

In a typical way, a solution of 30 mL CL (0.26 mole), 1.36 mL benzyl alcohol (0.013 mole) and 1.84 ml $\text{Al}(\text{OiPr})_3$ 0.71N (1.3 mmol) was slowly poured at the inlet of the extruder at various temperatures from 75 to 150°C . The residence times are regulated

by the screw rotation speed. The polymer was recovered at the outlet of the extruder and quenched in cold water.

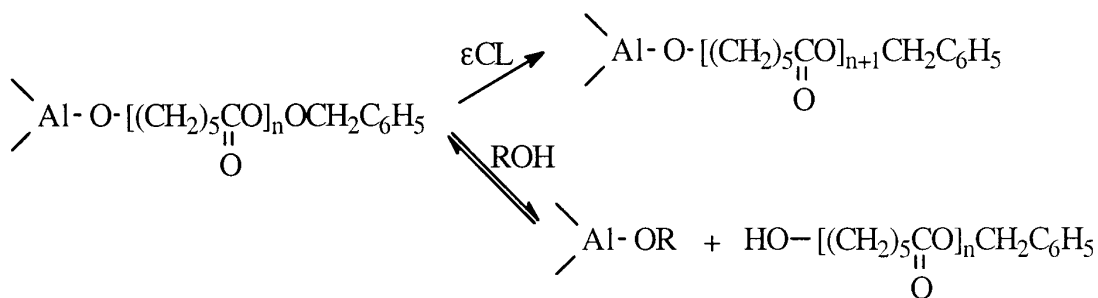
The polymer were characterized by NMR (Bruker spectrometer, 250 MHz), SEC (Waters pumps and refractometer with three columns Shodex) and Maldi-Tof mass spectrometry (Perkin Elmer Voyager DE STR apparatus, linear or reflector modes, calibration with Polyethylene oxide; matrix : indole acrylic acid / NaI).

Results and discussion

The transfer reaction

As outlined in the introduction, the key step in this polymerization is the transfer reaction which occurs when adding an alcohol in the reactional medium (scheme 1). This transfer reaction yields a polymer chain end-capped by an hydroxyl group which can further be used in another transfer reaction. If the alcohol is in excess with respect to the initiator, the average degree of polymerization is simply governed by the [monomer]/[alcohol ratio] (Eq.1). Provided the transfer reaction takes place more frequently than the propagation step, all the polymer chains are functionalized by the group issued from the alcohol (for instance the benzyl group when using benzyl alcohol) and a narrow molecular weight distributions can be expected [4].

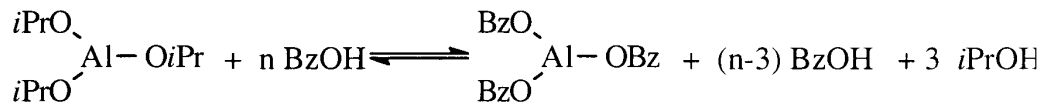
$$\overline{X}_n = \frac{[\text{Monomer}]}{[\text{Initiator}] + [\text{Alcohol}]} \rightarrow \frac{[\text{Monomer}]}{[\text{Alcohol}]} \quad (1)$$



Scheme 1. Propagation vs. transfer reaction in the ϵ -caprolactone polymerization

$\text{Al}(\text{O}i\text{Pr})_3$ has been chosen as the initiator because it gives rise to less side reactions than other initiators such as $\text{Sn}(\text{Oct})_2$ or $\text{Ti}(\text{O}i\text{Pr})_4$. $\text{Al}(\text{O}i\text{Pr})_3$ can react with benzyl alcohol to give aluminum benzylate (scheme 2). Consequently, ϵ -caprolactone polymerization can be initiated by both aluminum derivatives and the polymer chains are end-fitted either by isopropoxide or benzylate moieties. Using benzyl alcohol in excess with respect to $\text{Al}(\text{O}i\text{Pr})_3$ allows to neglect the polymer chains initiated by the

isopropoxide radicals.



Scheme 2. Formation of benzylate aluminum.

These polymerizations are usually carried out in solution in batch reactors at temperatures up to 60°C for 5 to 60 minutes, even during some hours, depending to the initiators. These experimental conditions are quite different from those encountered when using the extruder and it was of first importance to study in which way more severe experimental procedures could affect the functionality of the polymer chains as well as the molecular weight distribution. Therefore, we investigated polymerizations from different mixtures with temperature within the 75 – 150°C range.

The feasibility of the process has rapidly been established since polymerization occurs in all the above temperature range. The functionality of the polymer was checked both by ¹H NMR and Maldi Tof mass spectroscopy.

Functionality evidence

Figure 1 displays the NMR spectrum of the polymer obtained from the mixture described in the experimental section (in that case, the amount of Al(OiPr)₃ is 0,8 %wt). The temperature of the barrel was 150°C and the rotation speed of the screw was 10 rpm. This NMR spectrum clearly shows that the polymer chains are mainly end-capped by the benzyloxy group (resonance peak *b* at 5.11 ppm) issued from the benzyl alcohol. The very small resonance peak at 4.7 ppm, due to the hydroxybenzyl group clearly shows that very few free benzyl alcohol remains in the sample (the conversion is more than 95 %).

The difference between the intensities of the peaks at 5.11 ppm (*I_b* = 1.55) and 3.64 ppm (*I_{e'}* = 2.00) comes from the functionalization of some chains by the isopropoxy ligands brought by the initiator. This side reaction is also evidenced by the resonance peaks of the methyl groups at 1.23 ppm.

Since the three isopropoxy ligands are to be taken into account, the expected average number degree of polymerization issued from the mixture described in the experimental part will be :

$$\overline{X}_n(t) = \frac{[\text{Monomer}]}{3 \times [\text{Initiator}] + [\text{Alcohol}]} = \frac{0.26}{3.9 \times 10^{-3} + 0.013} = 15.4 \quad (2)$$

after the complete monomer consumption.

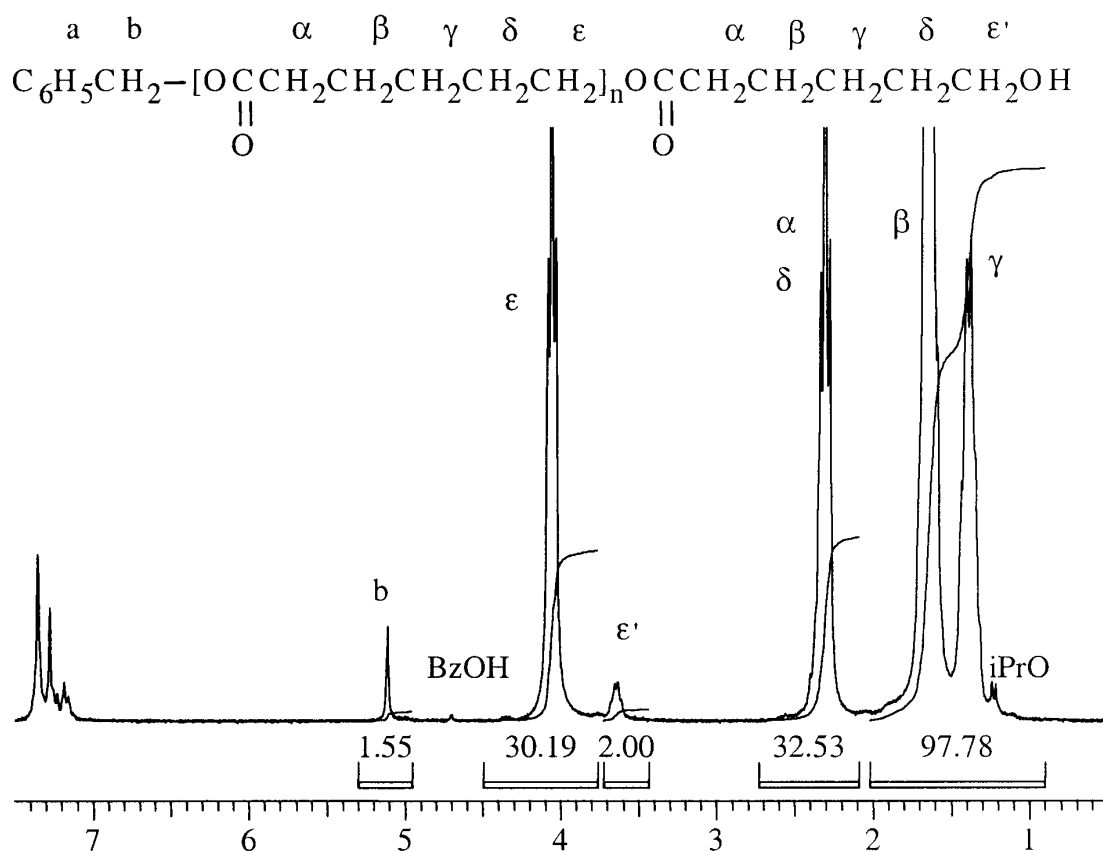


Figure 1. NMR spectrum of a benzyloxy polycaprolactone obtained at 150°C from the mixture described in the experimental part.

The actual average degree of polymerization can be determined from the relative intensities of protons belonging to the polymer chain (α or $\epsilon' + \epsilon$ are the most representative) and those assigned to the CH_2 end-group (peak ϵ'):

$$\overline{X}_n = \frac{I_\epsilon + I_{\epsilon'}}{I_{\epsilon'}} = 16.1 \quad (3)$$

Considering the only intensity of the benzyloxy group (peak b), that is neglecting the isopropoxy ligands, would lead to a

$$\overline{X}_n = \frac{I_\epsilon + I_{\epsilon'}}{I_b} = 20.8 \quad (4)$$

These results are in a good agreement with those expected. Taking into account the monomer conversion, the measured \overline{X}_n are slightly higher than those expected from the initial concentrations but the uncertainty is only about 5%.

Finally, the molar fraction of chains which are end-functionalized by a benzyloxy group is 77.5 %, to be compared to the theoretical value of 76.8 %. This result shows the efficiency of the transfer reaction in order to functionalize the polymer chains. The molar fraction of benzyloxy chains can be increased by decreasing the amount of isopropoxy aluminum. Using isopropanol as the transfer agent instead of benzyl alcohol will lead to 100 % chains being functionalized by isopropoxy groups. On the contrary, using the aluminum benzyloxy – benzyl alcohol combination will lead to 100% chains functionalized by benzyloxy groups. From a practical point of view, the question will be to find the minimum amount of commercially available aluminum isopropoxide required to get the complete consumption of monomer for the considered experimental procedure. A great number of reactions carried out in solution clearly showed that less than 10% of $\text{Al}(\text{OiPr})_3$ was necessary to get a good activity [11,12].

Some other experiments carried out from different initial mixtures gave us results with the same agreement, whatever the conversion. For instance, another polymerization was carried out from a mixture with a composition $\text{CL} / \text{BzOH} / \text{Al} = 40.1 / 1 / 0.1$ mole ($\text{Al}(\text{OiPr})_3 = 0.4$ wt %), keeping the same working conditions for the extruder. The NMR analysis of the polymer yields $X_n = 26.3$ and 35 by using Eq. 3 and 4 respectively, to be compared with the theoretical ones, namely 31 and 40.1. The conversion was found to be 85 %, indicating the residence time was too short in that case to get the complete monomer consumption.

Size exclusion chromatography

Figures 2 and 3 display SEC curves related to polymers obtained at 75 and 150°C from the same mixture. At low temperature (Figure 2), a bimodal distribution is observed with a shoulder in the high molecular weight domain. In that case, we found $\overline{M}_n = 3300$ g/mol with a polydispersity index $I = 1.32$. The attempt to adjust the molecular weight with the Mark Houwink Sakurada parameters, namely $k = 0.01395$, $a = 0.786$ [13] or $k = 0.0238$, $a = 0.757$ [14] yield $\overline{M}_n = 2240$ or 1870 g/mol respectively. The latter value is close to the theoretical one ($\overline{M}_n = 1863.6$ g/mol as determined from $\overline{X}_n = 15.4$). At higher temperature (Figure 3), the shoulder disappears, but the molecular weight distribution is broader : ($\overline{M}_n = 3540$ g/mol, $I = 1.55$; $\overline{M}_n = 2400$ g/mol after the MHS adjustment). The presence of the shoulder as well as the increase of the MWD at the higher temperature would imply that some high molecular weight species are present in the sample. This could be explained by the difficulty for the first transfer reaction to take place : polymerization starts rapidly from aluminum isopropoxide with a monomer insertion in the Al-OiPr bond and the exchange with benzyl alcohol occurs only in a second step. On the other hand, very low molecular weight species appear on the SEC curve related to polymerization at 150°C and neither NMR nor SEC can discriminate between oligomers or macrocycles.

Maldi-Tof mass spectrometry

Figures 4 and 5 display the Maldi-Tof mass spectra of two samples obtained from the

same mixture, but according to different working conditions. The first one was polymerized at 75°C at 30 rpm, while the second one was obtained at 150°C at 10 rpm. Values reported in both figures are assigned to the average mass (taking into account the isotopic distribution) of the $(M-Na)^+$ species Benzyloxy polycaprolactones

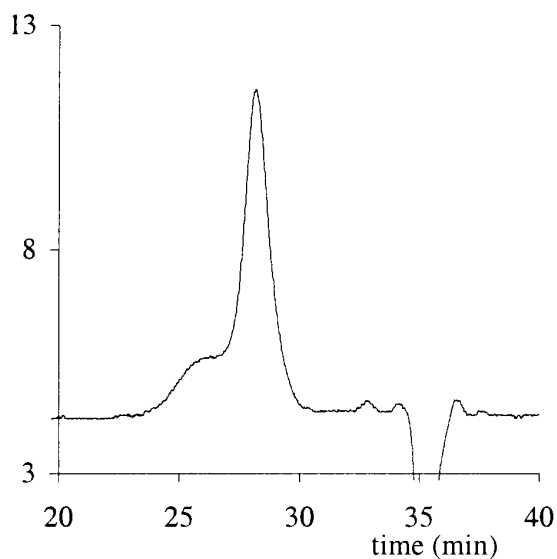


Figure 2. SEC of a sample obtained at 75°C.

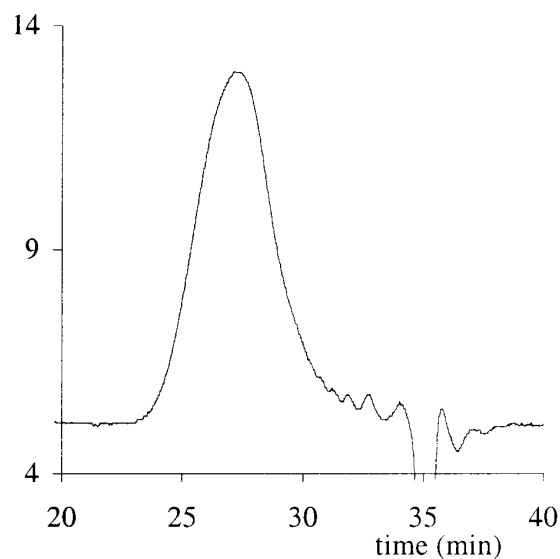


Figure 3. SEC of a sample obtained at 150°C, from the same mixture as in Figure 2.

are detected at $m/z = 114.115 \times n + 108.057 + 22.99$ while the isopropoxy species are detected at $m/z = 114.115 \times n + 60.096 + 22.99$. The accuracy is 0.05 %. For example, the peak detected at $m/z = 1843$ is assigned to a macromolecule with $n = 15$ units.

The peaks at $m/z = 1910.2$, 2024.5 in Figure 5 are due to the chains functionalized by an isopropoxy end-group. At higher temperatures, the rate of insertion in the Al-O bound would be higher and the first exchange between benzyl alcohol and aluminum isopropoxide does not occur. Nevertheless, this drawback can be circumvented by using a higher alcohol/aluminum ratio. Finally, there is no clear evidence of macrocycles in the low molecular weight domain. The molecular weight distribution (MWD) can also be determined according to Eq. 5 and 6. The intensity h_i of each peak is proportional to the number n_i of chains of the same length, with the same proportionality constant in the whole range of molecular weights. It must be recalled that this assumption remains valid only in the case of narrow MWD. The average molecular weight deduced from Figure 4 is $\bar{M}_n = 2000$ g/mol. The polydispersity index is $I = 1.1$. Although an apparent broader molecular weight distribution in Figure 5 (with the same \bar{M}_n), the polydispersity remains low, around 1.2. In both cases, the MWD are narrower than those obtained from SEC measurements. The MWD of these samples is actually too broad to allow a good characterization by Maldi-Tof mass spectrometry.

However, whatever the actual MWD, it remains below than those previously reported [9,10].

As a conclusion, the bulk polymerization of ϵ -caprolactone in a mini-extruder in the presence of a transfer agent is a versatile tool to give directly functional oligomers with a controlled MWD. The amount of functionalized polymer chains depend directly on the transfer agent / initiator ratio. The main species are the expected

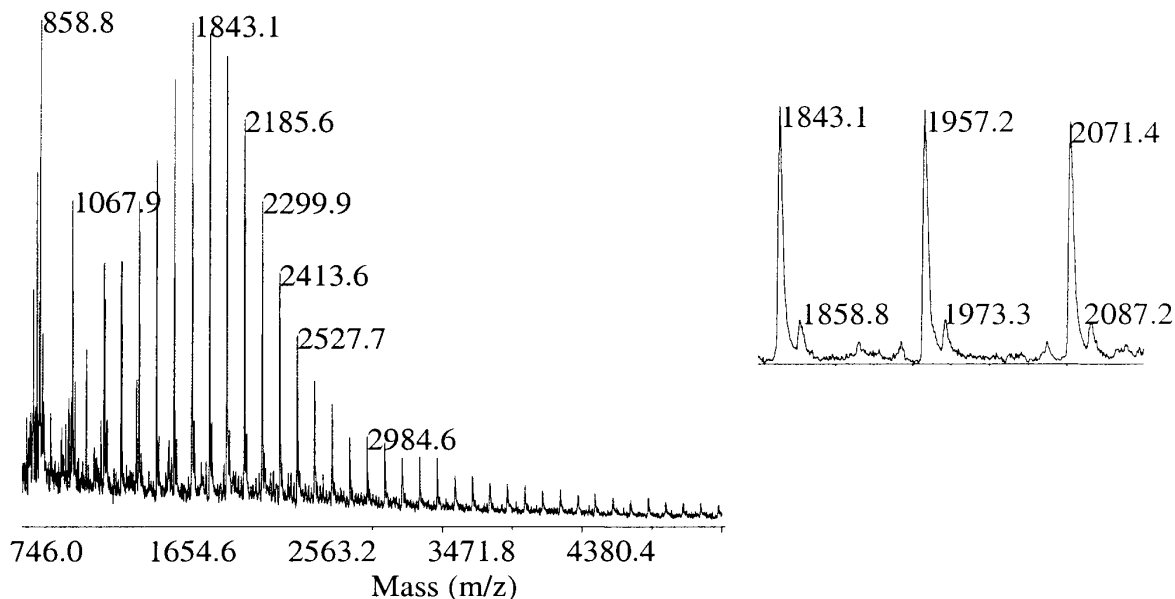


Figure 4. Maldi-ToF mass spectrometry of the sample obtained at 75°C at 30 rpm. The peaks at $m/z = 1858.8, 1973.3 \dots$ are assigned to the species $(M-K)^+$.

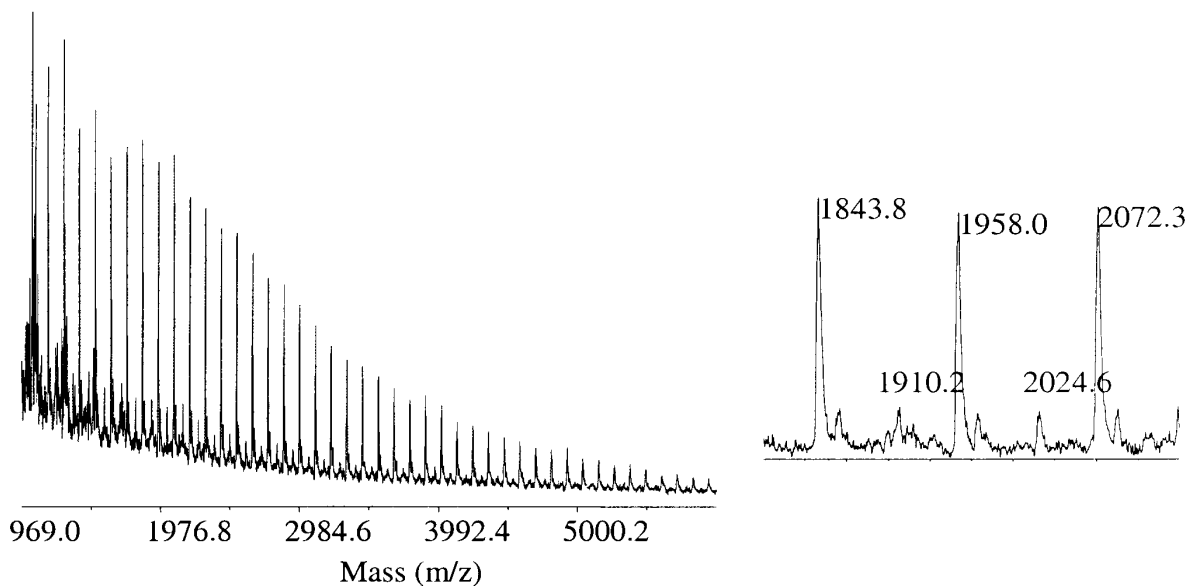


Figure 5. Maldi-ToF mass spectrometry of a sample obtained at 150°C at 10 rpm.

$$\overline{M}_n = \frac{\sum M_i \times n_i}{\sum n_i} = \frac{\sum M_i \times h_i}{\sum h_i} \quad (5)$$

$$\overline{M}_w = \frac{\sum M_i^2 \times n_i}{\sum M_i \times n_i} = \frac{\sum M_i^2 \times h_i}{\sum M_i \times h_i} \quad (6)$$

benzyloxy end-capped oligocaprolactones and no macrocycles have been detected by mass spectroscopy.

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