Nature of a Low Molar Mass Peak in Anionic Poly(ε-caprolactam). Main Aspects of Its Formation

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ABSTRACT: Macrocycle formation, typically from M_7 to M_{20}, in anionic polycaprolactam (PCL) has been thoroughly investigated by running the anionic synthesis of PCL in different experimental conditions. Reaction parameters have been changed, paying special attention to avoid conditions that can favor the formation of side products during the anionic polymerization of ϵ-caprolactam (CL). Namely, all syntheses have been performed in isothermal conditions. Formation and content of macrocyclic PCL have been evaluated as functions of polymerization time as well as activator nature and concentration. Considering that anionic PCL formation is a kinetically controlled process, the present work has been also aimed to investigate the content of both low mass cyclic and macrocyclic species after prolonged thermal treatments (annealing tests) in order to analyze our data in terms of thermodynamic equilibrium. High molar mass cyclic oligomers (M_7-M_{20}) have been monitored by size exclusion chromatography (SEC) and MALDI mass spectrometric analysis, while high performance liquid chromatography (HPLC) has been helpful for a quantitative evaluation of lower molar mass species. On the basis of our results, possible mechanisms of macrocyclic PCL formation have been proposed.

Introduction

Cyclic species are surprisingly common among the products of several polymerization reactions, namely in polycondensation and in ring-opening polymerization of heterocyclic monomers. Step-growth polymerizations almost invariably lead not only to a sizable fraction of low molar mass cyclics but also, besides linear chains, to an appreciable amount of rings[1,2] in the high molar mass fraction.

In the ring-opening polymerization of ε-caprolactam (CL), low molar mass cyclic oligomers (M_x, with $x \leq 8-9$) are considered an unavoidable outcome in either the hydrolytic or the anionic route, negatively affecting properties and performances of the obtained PCL. Extensive extractions by suitable solvents (typically hot water, often containing low-mass lactamic fractions) are carried out in industry in order to remove as many M_x species as possible from the polymer before utilization.

However, it has recently been shown by DSM researchers[3] and further verified by our previous work of this series[4] that the usual extraction techniques of oligomers by boiling water or methanol are not at all able to remove the whole oligomeric fraction: only the lowest species (monomer, dimer, and trimer) are fully extracted. Even tetramer extraction is not complete, and the solubility of higher cyclic fractions (from pentamer to nonamer) is becoming lower and lower in the extraction media. The actual concentration of higher cyclic oligomers ($x \geq 5$) largely exceeds the amounts usually taken for valid in most literature works. Since all quoted values for cyclic species have been obtained by Soxhlet extraction with the above solvents, it is reasonable to assert that a very large part of the existing studies on ring-chain data for PCL, and in particular for anionic PCL, have to be ruled out.

On the basis of the above considerations, the evaluation of individual cyclics in our laboratory-made samples, traditionally accomplished by analyzing the extraction products, has been focused on the development of new techniques that do not require any previous separation from the high polymer fraction. Namely, the identification of cyclic oligomers in the reaction products has been made considerably easier by taking advantage of MALDI-TOF mass spectrometry that, in the case of PCL, enables to detect individual cyclic and linear species with no limitation in terms of molar mass and end groups.[2,5–8] Indeed, thanks to this technique, it has been possible[4] to find in fast anionically polymerized PCL that, besides the well-known trend of cyclic oligomer distribution decreasing from dimer to hexamer, a previously unknown fraction of macrocyclics (the so-called GR peak), rising from M_{7-9} up to M_{20-25} or higher as functions of the experimental conditions, is present. It is also worth mentioning that, recently, SEC/HPLC chromatography has found application in quantitative detection of polyamide oligomers directly on polymer sampling without extraction. Namely, relevant works, published by the aforementioned DSM research group, deal with both the analysis of the first six linear and cyclic oligomers of PCL by liquid chromatography, using the sandwich injection method,[3,9,10] and the analysis of higher oligomers on a silica-based reversed-phase column with a gradient of formic acid or hexafluoroisopropanol in water.[11]

Historically, and long before the availability of reliable experimental data, an elegant theory of cyclization has been put forward by Jacobson and Stockmayer,[12] who evaluated the probability that a single linear chain can form a ring; the ring−chain equilibria, under thermodynamic conditions, can be calculated as functions of concentration, chain stiffness, and conversion. The Jacobson−Stockmayer (J−S) theory has been

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applied later on to hydrolytic PCL using the RIS model of Flory and Williams,[13] and the content and composition of cyclic oligomers have been calculated and compared to the experimental values,[14–17] at present known as erroneous because of the incomplete solvent extractions, as discussed above. More recent works, related to the content of cycles and macrocycles in aliphatic polyamides, evaluated by modern analytical techniques such as MALDI-TOF mass spectrometry have been published by Kricheldorf and co-workers. Namely, polyamide cyclization has been studied either in thermodynamically controlled polycondensations (for PCL)[2] or in kinetically controlled polycondensations (polyamides of some specific aliphatic dicarboxylic acids).[18]

Conversely, cyclic oligomer formation in anionic PCL has been studied by only a few authors[19–23] essentially following the experimental trends. No theoretical approach has been put forward for the cyclization reaction mechanism in the anionic polymerization route.

Theories limited to thermodynamically controlled step polymerizations cannot be helpful to explain the macrocyclic *ensemble* recently discovered in anionic PCL[4] and deeply explored in the present paper. Indeed, it is worth mentioning again that anionic polymerization of PCL, initiated at relatively low temperature by very fast chain initiators (activators) as in our case, is a kinetically driven chain polymerization.

As a matter of fact, although the anionic polymerization of lactams has been studied quite extensively since the seventies of the past century,[24–28] both the complex chemistry and the detailed mechanism of all feasible reactions involved have not yet been fully and definitively clarified. The reason most probably resides in the simultaneous presence of many side reactions, caused by both the strong basicity of the medium and the high polymerization temperatures, leading to extensive PCL branching or even cross-linking together with the formation of many structural irregularities and byproduct.

Some more recent studies on the activated anionic polymerization of ε-caprolactam in quasi-adiabatic conditions, carried out in the 1990s,[29–31] together with new findings of our research group[32,33] allowed to overcome the above complexity. These latter have shown that, if the anionic polymerization is carried out in quasi-isothermal conditions at relatively low temperatures (ca. 150 °C) by very fast chain initiators, PCL almost completely free of structural defects and side products is produced in very high yields. In the above conditions, the polymerization product is characterized by higher molar masses and narrower polydispersities.[34] In this scenario where a "clean polymerization", very limited in side reactions, is involved, more accurate evaluations of relative and absolute contents of rings and linear chains can be properly achieved.

It is also worth noting at this point that, in the activated anionic polymerization of CL, a chain reaction mechanism is involved, and PCL end groups substantially differ from those of hydrolytic poly(ε-caprolactam). The residue of the fast monofunctional activator (e.g., cyclohexylcarbamoylcaprolactam) is present at one end of the polyamide chain while, at the other, acyloylcaprolactam is the persisting active center. Although a certain level of reversibility of the propagation reaction has to be taken in account, the active center might be able to propagate indefinitely; if no chain transfer or termination occurs, a "living-reversible" polymerization may be attained.[35]

Some broadening of the PCL molar masses (as referred to monodispersity) found experimentally[34] is linked to the above reversibility and, in addition, to transamidation reactions prevalently occurring in the final stages of the process. Among the latter reactions, cyclization of PCL chain molecules is obviously in competition with polymer growth and can represent a relevant source of termination reactions.

As mentioned above and detailed in our previous study,[4] we have also found in fast anionically polymerized PCL sample that in addition to the lower cyclic oligomers, whose content is regularly decreasing from dimer to hexamer, a sizable fraction of macrocyclics from heptamer−nonamer to M_{20-25} or higher are present. These low mass polymerization products, detected as a characteristic peak in SEC traces (so-called GR peak), have been characterized by a new selective precipitation procedure and fully identified by the MALDI-TOF technique. It has been shown that the GR peak represents about 3 wt % of the whole polymer yield.

In the present paper, a deeper insight into the relevance of macrocyclic species content as a function of experimental conditions, together with an attempt to identify possible mechanisms of their formation, is put forward. An analysis of macrocyclic fraction content in annealed anionic PCL samples is also shown.

Experimental Section

Synthesis of Anionic Polyamide 6. Anionic PCL samples were laboratory preparations synthesized by fast-activated anionic polymerization of CL, following the procedure already described[4,32] for the isothermal bulk polymerization. Sodium caprolactamate (NaCL) was the initiator of the polymerization, and cyclohexylcarbamoylcaprolactam (CCCL) and hexamethylene dicarbamoylcaprolactam (HCCL) were chosen as monofunctional and bifunctional activator, respectively. Polymerization temperature was 155 °C for all the samples.

Synthesis of Hydrolytic Polyamide 6. Hydrolytic PCL samples were synthesized at high temperature (270 °C) using an aluminum block heated by electric resistors connected to a rheostat. A mixture of CL (9.70 g), ε-aminocaproic acid as initiator (0.40 g), and water (0.50 g) was introduced into a glass polymerization vessel at room temperature and heated up to the polymerization temperature by placing the vessel in the aluminum block for 4 h. At the end of the reaction, the vessel was rapidly cooled to room temperature under a continuous stream of nitrogen.

Annealing of PCL. The annealing of anionic PCL was performed in a glass vessel, under nitrogen stream, at different temperatures and for different times: (i) 180 °C/48 h, (ii) 200 °C/48 h, and (iii) 250 °C/24 h (reduced time in order to avoid extensive polymer degradation).

Measurements. SEC runs were carried out on a liquid chromatograph, equipped with a Waters CUM column heater, a Waters 2690 separation module, a Waters 2410 refractive index detector (RID), and a Waters 996 photodiode array detector (PDA). 1,1,1,3,3,3-Hexafluoro-2-propanol (HFIP) containing 0.01 M tetraethylammonium nitrate (TEAN) was used as eluent (sample concentration 2 mg/mL) at 35 °C with a flow rate of 0.5 mL/min. PDA, settled at the wavelength of 215 nm, as well as RID was used. Three Zorbax PSM Bimodal-S columns (6.2 × 250 mm, 5 μm) were chosen for this analysis. Molar masses were calculated with reference to poly(methyl methacrylate) (PMMA) standards.

HPLC runs were performed with the same instrumentation used for SEC chromatography. Eluent: a 40/60 vol mixture of 2,2,2-trifluoroethanol (TFE)/H_2O; column: Lichrosorb RP-8 (4.6 × 250 mm, 5 μm); column heater temperature: 30 °C; flow rate: 0.9 mL/min; detector: PDA settled at 210 nm. Two calibration curves were performed, using CL and its cyclic dimer, respectively, as external standards.[36] The samples for this analysis were prepared by selective precipitation as follows: 1 g of sample was dissolved in 40 mL of TFE. Then, the solution was slowly added to 100 mL of methanol under stirring and the precipitate was filtered. The clear solution was dried by solvent removal in rotovapor.

Positive MALDI-TOF mass spectra were acquired by a Voyager DE-STR (Applied Biosystems, Foster City, CA) using simultaneously a delay extraction procedure (25 kV applied after 2600 ns with a potential gradient of 454 V/mm and a wire voltage of 25 V) and a detection in linear mode. The instrument was equipped with

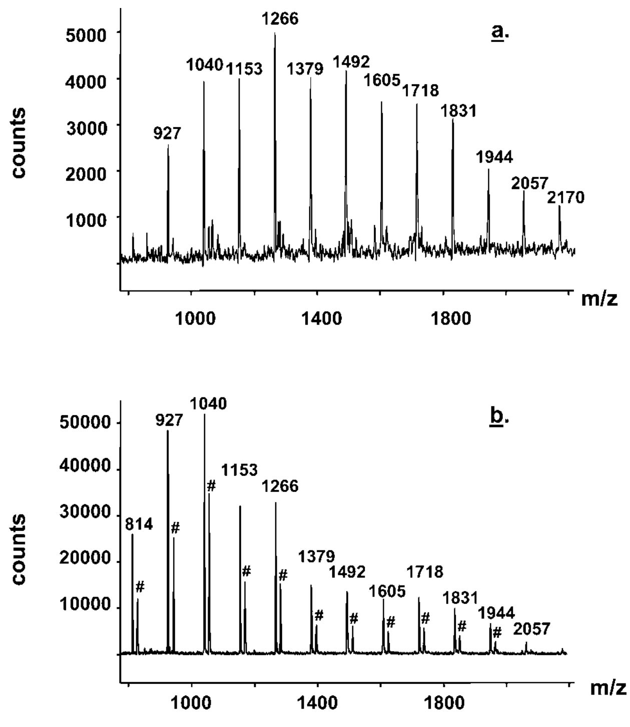


Figure 1. MALDI-TOF mass spectra of the sample F22 "as-polymerized" (a) and of the GR peak species obtained by fractionation of the sample F22 (b).

a nitrogen laser (emission at 337 nm for 3 ns) and a flash AD converter (time base 2 ns). *trans*-3-Indoleacrylic acid (IAA) was used as the matrix; the mass spectrometer calibration was performed as previously reported.[37] Because of the isotopic composition, molecular species are detected in the mass spectra as clusters of peaks; to simplify their assignments, *m/z* values reported on the spectra and in the text are referred to the first peak of each cluster, corresponding to the ion containing the most abundant isotope of each element present.

Results and Discussion

Prior to the presentation and discussion of the results of our work, it is necessary to spend a few words on the characteristics of the samples chosen to investigate macrocycle formation. Indeed, in our previous paper of the series,[4] anionic PCL by fast-activated suspension polymerization in quasi-isothermal conditions has been considered, and its fraction corresponding to the GR peak has been analyzed after separation; conversely, in the present paper we have chosen to synthesize PCL samples by fast-activated isothermal polymerization in bulk, and no previous purification or fractionation process has been performed. The above strategy is justified by two reasons:

(i) First of all, we have been interested to verify the effectiveness of the fractionation process described in our previous paper[4] and used to identify the species forming the GR peak. For this purpose, the MALDI spectrum of the sample F22[32] "as polymerized" in bulk (Figure 1a) has been compared to the spectrum of its fraction corresponding to GR peak species (Figure 1b). The peaks of the two spectra in the range between 800 and 2400 Da, confirming that the method used to separate macrocycles from the high polymer does not lose any species in the above range of molar masses; however, the distribution curve of macrocycle content in the two samples is clearly different, thus suggesting that the fractionation method we used to isolate the GR peak was not fully quantitative and that a small fraction of cycles higher than M_9 do not remain in solution and are separated together with the high polymer. Therefore, we can conclude that it is more appropriate to pursue our work on macrocyclic species in PCL anionic polymerization by analyzing the samples without any purification and fractionation. (ii) Moreover, the PCL samples of the present work have been obtained by fast anionic polymerization in bulk, not in suspension, to avoid any presence of impurities entrapped in PCL powders, which could generate additional spurious peaks. The excellent correspondence of the two polymerization approaches in terms of PCL molar mass, already shown[4] by comparing SEC traces of F22 (polymerization in bulk) and LR9 (polymerization in suspension), has been further verified in the present work matching MALDI traces of the two samples (spectra not given).

Table 1. Conditions of PCL Synthesis[a]

sample code	activator	activator concn (mol %)	t_{pol} (min)
F22	CCCL	0.6	10
S48	HCCL	0.3	10
S45	CCCL	1.2	10
P35	CCCL	0.6	5
P36	CCCL	0.6	3

[a] Initiator: NaCL, in equivalent concentration; T_{pol}: 155 °C.

As discussed in the Introduction, our study aims to get a deeper insight into PCL macrocyclics trying, on one hand, to identify the experimental parameters that control their formation and, on the other, to hypothesize some mechanisms of their production. For this specific reason, some samples of anionic PCL have been synthesized in different conditions by changing a few reaction parameters, still paying great attention not to favor the side reactions described in the literature.[24–26] Indeed, the possible presence of side products characterized by relatively high molar mass, besides the macrocyclics of our interest, could lead to relevant misinterpretation of experimental data. Moreover, a polymerization pathway affected by side reactions (such as Claysen-type condensations) should strongly mask possible mechanisms of GR peak formation, making more difficult to explain it. A full picture of experimental conditions used for the synthesis and the characterization of various PCL samples is given in Table 1.

Two PCL samples have been prepared by using a couple of fast activators (one monofunctional, the other bifunctional), both able to polymerize ε-caprolactam in an almost complete absence of side reactions, provided that the polymerization temperature (T_{pol}) is kept rather low (155 °C). The sample F22, obtained by the monofunctional activator CCCL, has been compared to the sample S48, synthesized in the same conditions by HCCL (bifunctional activator). Such comparison can be used in order to investigate whether the nature of activator (mono- or bifunctional) can affect macrocycle formation, i.e., to evaluate the possible role of a large molar mass increase of PCL and related increase of medium viscosity, as in the case of bifunctional activation,[32] on GR peak extent and composition. SEC chromatography traces of the above samples of anionic PCL (Figure 2) show, indeed, a sharp difference in high polymer molar mass only, while the GR peak for both samples comes out at almost the same elution time and has a very similar shape. A deeper analysis of both GR peaks has been performed by the MALDI-TOF technique, and the spectra of S48 (Figure 3) and F22 (Figure 1a) have been compared. In both spectra, a series of intense peaks corresponding to the sodiated ions of cyclic oligomeric species, having a repetition unit of 113 Da, are observed at *m/z* values of (n113 + 23) in the mass range of 800−2400 Da. Less intense peaks due to protonated (M_nH^+, at n113 + 1, indicated as ●) and potassiated (M_nK^+, at n113 + 39, indicated as ×) ions of the same cyclic oligomers also appear in the spectrum of Figure 3. Accordingly, it can be deduced that also when a bifunctional activator is used, the GR peak is composed by cyclic oligomers of PCL only. Comparing the

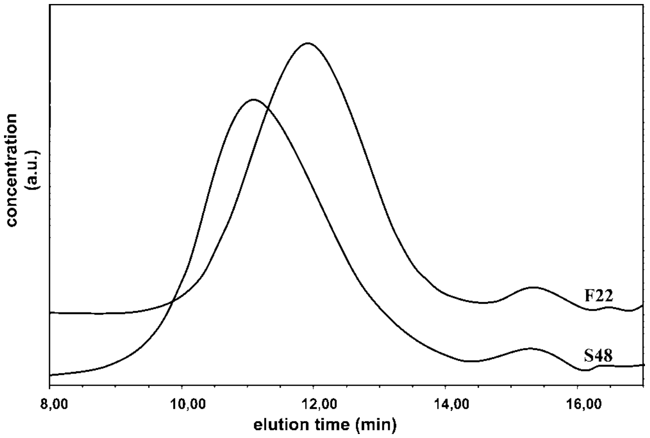


Figure 2. SEC traces of the sample S48 (activator HCCL) and F22 (activator CCCL).

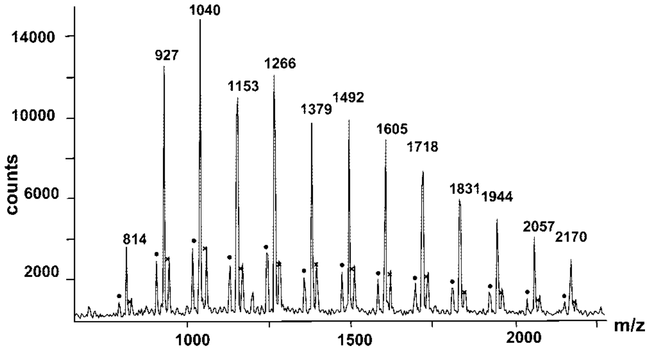


Figure 3. MALDI-TOF mass spectrum of the sample S48.

spectra of Figure 1a and Figure 3, it can be observed that the latter activator provides a slightly different distribution of the cycles, characterized by a maximum at 1040 Da (M_9).

It is also interesting to take into account the possible influence of another relevant polymerization parameter: the reaction rate, which can be modified by changing the concentration of activator. As specified in our previous papers,[4,32] the need to work in an almost complete absence of side reactions limits the possibility of exploring synthetic conditions too different from the most suitable ones, corresponding to 0.6 mol % of monofunctional activator referred to CL. For the same reason, it is important as well not to modify the (1:1) functional group ratio between activator and initiator.

On this basis, the sample S45 has been synthesized by using a 1.2 mol % of both CCCL activator and NaCL initiator. This specific concentration is different enough from the reference value (0.6 mol %) to allow us to appreciate a possible influence of the polymerization rate on macrocycle formation, but not so different to favor a sizable presence of side reactions. Conversely, an activator content of 0.3 mol % has not been considered suitable for our purposes, as a sharp decrease of the polymerization rate (i.e., increase of polymerization time, t_{pol}) would be inevitably accompanied by a very large formation of Claisen-type condensation reactions.

The SEC chromatogram of sample S45, given in Figure 4, has been compared with that of F22; the difference in terms of high molar masses of the two PCL samples is evident, while no appreciable change is observed for the GR peak. The MALDI spectrum of S45, not reported, confirmed that the GR peak is composed by cyclic oligomers of PCL only, characterized by the same distribution shown by the sample F22 (maximum at 1266 Da, M_{11}).

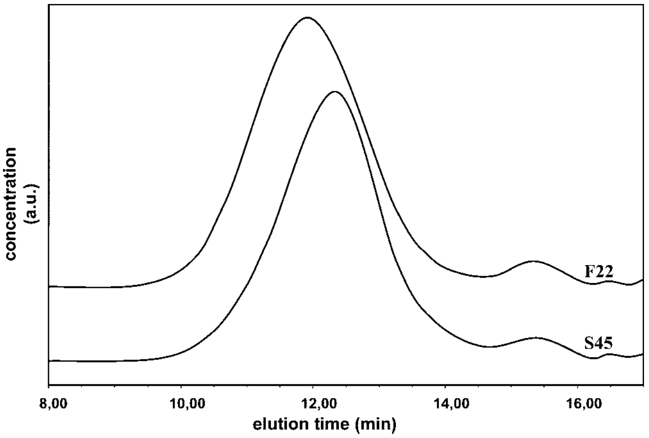


Figure 4. SEC traces of the sample S45 (CCCL concentration: 1.2 mol %) and F22 (CCCL concentration: 0.6 mol %).

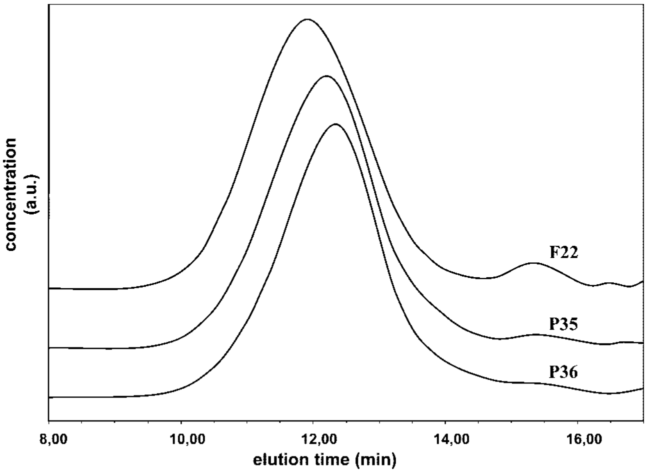
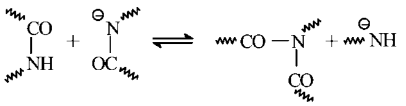


Figure 5. SEC traces of the sample P36 (t_{pol}: 3 min), P35 (t_{pol}: 5 min), and F22 (t_{pol}: 10 min).

In light of the above data, a couple of anionic PCL samples have been prepared by stopping the polymerization at lower times in order to find out whether macrocycle formation is linked to the high polymer content in the reacting mass or is based on an independent mechanism. P35 and P36 have been synthesized in only 5 and 3 min, respectively, and compared to F22, characterized by a t_{pol} of 10 min.

The SEC curves (normalized) of the three samples are shown in Figure 5. The area of the GR peak is directly dependent on t_{pol}, since it appears to be strongly reduced when t_{pol} is 3 min only and the high polymer yield is ca. 40 wt %. At $t_{\text{pol}} = 5$ min the area of GR peak is still rather small. The above result underlines that, although the macrocycle formation takes place during the entire polymerization process, its relevance is remarkable only at medium−high conversions. Moreover, it can be inferred that its formation is linked to some very fast mechanisms, presumably different from the classical one proposed for the low mass cyclic oligomers and mostly consisting in transamidation reactions.[19,20] The above chromatograms give also some interesting information on the high polymer, showing a regular increase of the molar mass as a function of t_{pol}. This behavior could be due, in our opinion, either (or both) to (i) the quasi-living character of anionic CL polymerization when side reactions are strongly limited or (and) (ii) the presence of a few branched chains formed because of the high basicity of the reacting medium, on the basis of some (relatively slow) reactions centered on PCL anionic species formed by proton abstraction from the polyamide chain, as reported in the following four examples taken from the literature: [24–26]



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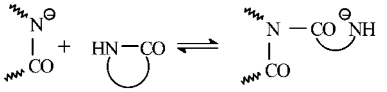

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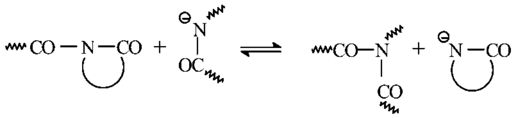

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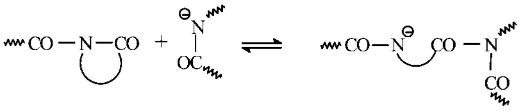


(4)

At present, it is not possible to identify between the two above-mentioned possibilities, which is the main factor of high polymer molar mass increase as a function of polymerization time.

An investigation on the composition of GR peak as a function of t_{pol} has been carried out by monitoring the MALDI traces of P35 and P36 in comparison with that of F22, already given in Figure 1a. The GR peak data for $t_{pol} = 3$, 5, and 10 min are shown in Figure 6. The same family of peaks, due to cyclic oligomers cationized as sodiated species, is observed in all spectra at m/z values of (n113 + 23), but by comparison among the registered counts, the gradual increase of the absolute abundance of ions can be observed as t_{pol} increases. At the same time, the most abundant oligomeric species present in the GR peak change from M_8 (peak at m/z 927, Figure 6a) to M_9 (peak at m/z 1040, Figure 6b) and M_{11} (peak at m/z 1266, Figure 6c).

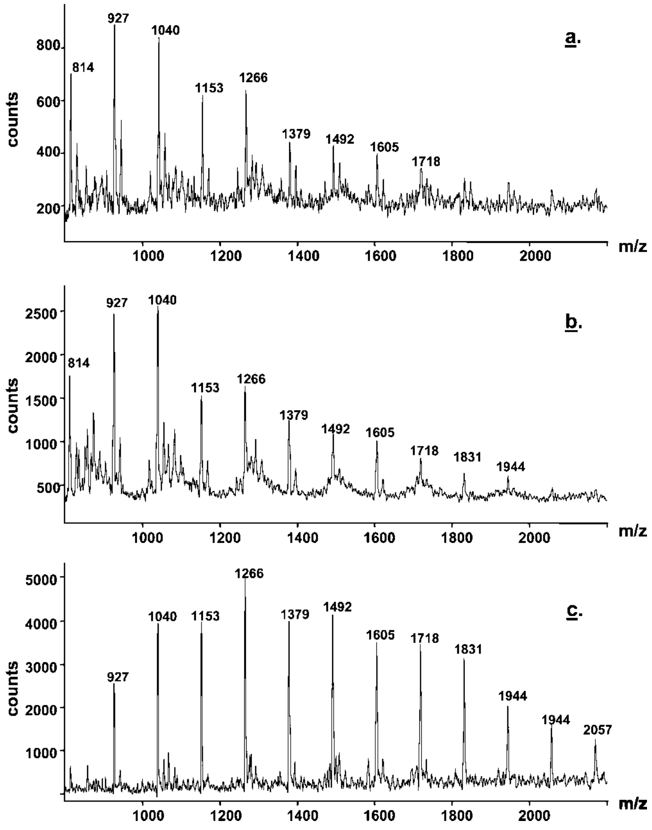


Figure 6. MALDI-TOF mass spectra of the sample P36 (t_{pol}: 3 min) (a), P35 (t_{pol}: 5 min) (b), and F22 (t_{pol}:10 min) (c).

MALDI analysis has also been useful in order to perform a comparison between a hydrolytic PCL sample (Figure 7) and the anionic PCL coded F22, in the range of 800−2500 Da, where the GR peak usually appears. As expected, the hydrolytic sample shows the presence of two homologous series constituted of cyclic (peaks at m/z n113 + 1, indicated as ×) and linear (peaks at m/z n113 + 19, indicated as ●) oligomeric species. Differently from the previous MALDI spectra (Figures 1, 3, and 6), all species detected in this latter spectrum are essentially protonated ions (as a consequence of their different origin). It can be observed that the abundance of the cyclic species, with respect to the linear ones, is higher at low masses than at high masses. Moreover, both series, in the interval ranging from M_7 up to M_{22}, show a regularly decreasing trend as functions of increasing molar mass, quite different from the peak behavior observed in the case of anionic samples. On the other hand, also SEC traces underline the differences between anionic PCL samples (GR peak) and hydrolytic ones (a more or less extended step, SEC trace not given).

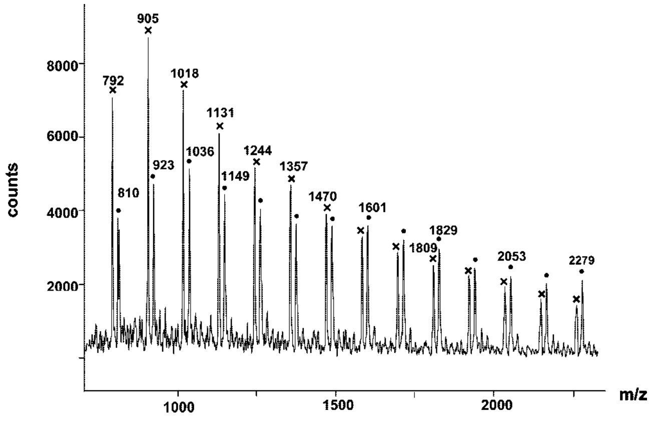


Figure 7. MALDI-TOF mass spectrum of a PCL sample obtained by hydrolytic mechanism.

As already foreseen in the Introduction, macrocycles forming the GR peak are species generated under strict kinetic control: in our opinion, some interesting information could be obtained by analyzing anionic PCL after suitable annealing tests aiming to approach thermodynamic equilibrium.

In light of these considerations, the sample F22 has been first extracted with methanol in order to remove, at least in part, lower mass cyclics and subsequently annealed at temperatures and for times considered in the literature adequate to approach thermodynamic equilibrium. Namely, two annealing tests have been performed below PCL melting temperature (at 180 and 200 °C, respectively) for 48 h, as suggested in the literature,[19,20] while the third test has been performed on molten PCL (at 250 °C) for 24 h only, since PCL thermal degradation had to be avoided or minimized. Cyclic oligomers with molar masses in the range of M_1−M_7 and higher molar mass species have been analyzed separately by the two different techniques described in the Experimental Section.

Low molar mass oligomers have been detected by HPLC analysis, after the extraction procedure. The quantitative evaluation of each species is shown in Table 2 as a function of the annealing conditions and in comparison with the "as-polymerized" and the extracted samples. Contrary to what we expected on the basis of previous experimental data,[19,20] the results suggest that only annealing on molten PCL (at 250 °C) induces detectable changes in the content of low molar mass cyclic oligomers. When annealing on solid PCL is performed, the content of the above oligomers does not change, except for the

Table 2. Cyclic Oligomer Concentration, [M$_x$] (wt %), in F22 before and after Annealing

x	[M$_x$]^a	[M$_x$]^b	[M$_x$]^c	[M$_x$]^d	[M$_x$]^e
1	1.51	0	0.06	0.07	0.08
2	0.40	0	0	0	0.04
3	0.13	0	0	0	0.08
4	0.09	0.01	0.01	0	0.07
5	0.08	0.02	0.02	0.02	0.07
6	0.11	0.08	0.06	0.07	0.14
7	0.11	0.09	0.08	0.09	0.10

[a] F22 as polymerized. [b] F22 extracted by methanol. [c] F22 after annealing at 180 °C for 48 h. [d] F22 after annealing at 200 °C for 48 h. [e] F22 after annealing at 250 °C for 24 h.

formation of a slight amount of ε-caprolactam. This unexpected resistance of the polymer to a molecular re-equilibration should be attributed to (i) the very high extent of the crystalline phase, typical of anionic PCL obtained by ultrafast activators in isothermal conditions, and/or (ii) the full removal of any trace of catalytic species (such as sodium caprolactamate and blocked isocyanates), able to favor cyclization, due to the highly efficient extraction of ground polymer with methanol.

Full information to explain the noncorrespondence between our results and Reimshuessel's data[19] could be obtained by performing additional annealing tests on both hydrolytic and anionic PCL, this latter obtained from a slow activator, following the same procedure adopted for our samples. These experiments are in progress and will be published elsewhere.

The fractions made of higher molar mass species in annealed samples have been detected by the MALDI-TOF technique in the range between 800 and 2200 Da and compared in Figure 8. The spectrum of F22 after extraction by methanol is not reported herein because of its full correspondence to the spectrum of "as-polymerized" F22 (Figure 1a). It can be observed that all macrocycles forming the GR peak are present with analogous distribution in every annealed sample: expected modifications, at least at strong annealing conditions (250 °C), did not occur. However, it is dutiful to underline the nonquantitative character of MALDI analysis in our experimental conditions, namely without a suitable internal standard. For this reason, a study to improve MALDI experimental conditions with the aim of getting a quantitative evaluation of each detected species is in progress. It is also likely that high cycles need longer times at high temperature to undergo detectable changes toward a distribution controlled by thermodynamic parameters, even though caution should be always kept in mind when performing annealing under too strong conditions because of the phenomenon of thermal degradation of the polymer.

On the basis of the above results, it is our opinion that some hypotheses of mechanism can be suggested in order to explain the formation of macrocycles corresponding to the GR peak, at least in the fast anionic polymerization of CL. In particular, we consider that two mechanisms are in good agreement with the results of the present paper.

The first mechanism (Scheme 1) consists of the well-known (intra- or intermolecular) transamidation reactions in order to explain the formation of lower mass cycles in the case of hydrolytic as well as anionic polymerization. This is the simplest mechanism of cycle formation, since transamidation reactions are always involved, especially in the latter stages of polymerization. However, the main drawback of this pathway, involving an intermolecular reaction, is the compulsory presence of two simultaneous interchange reactions to generate a cycle. Furthermore, the transamidation kinetics at this T_{pol} is relatively slower, as compared to the main polymerization, analogously to what happens to the side reactions.

The second proposal, shown in Scheme 2, is less classical and has been inspired to us by a work of Ueda et al.[22] where, for the first time, a mechanism for cyclic dimer and trimer formation in anionic polymerization of ε-caprolactam has been discussed. In this pathway, a ionized amide bond, produced by H$^+$ abstraction, is believed to be present along the linear growing chain. We have already listed some possible (although minimal in our experimental conditions) branching reactions originated by such anionic species, whose formation is highly probable as is consistent with the high basicity of the reaction medium. Also, the transamidation Scheme 1, already discussed, is based on the same species. If chain conformation allows the $-\mathrm{N}^-$ anion to approach its chain end (cyclic imide), the anion is capable of a nucleophilic attack, in competition with the lactam anion, to the imide end group to generate a loop. The resulting N-acyl cyclic species would next undergo attack by the monomer anion and would form a cyclic oligomer and a linear chain. This pathway has the advantage over the previous one to be unimolecular only. GR peak formation can be prevalently attributed, in our opinion, to this backbiting process.

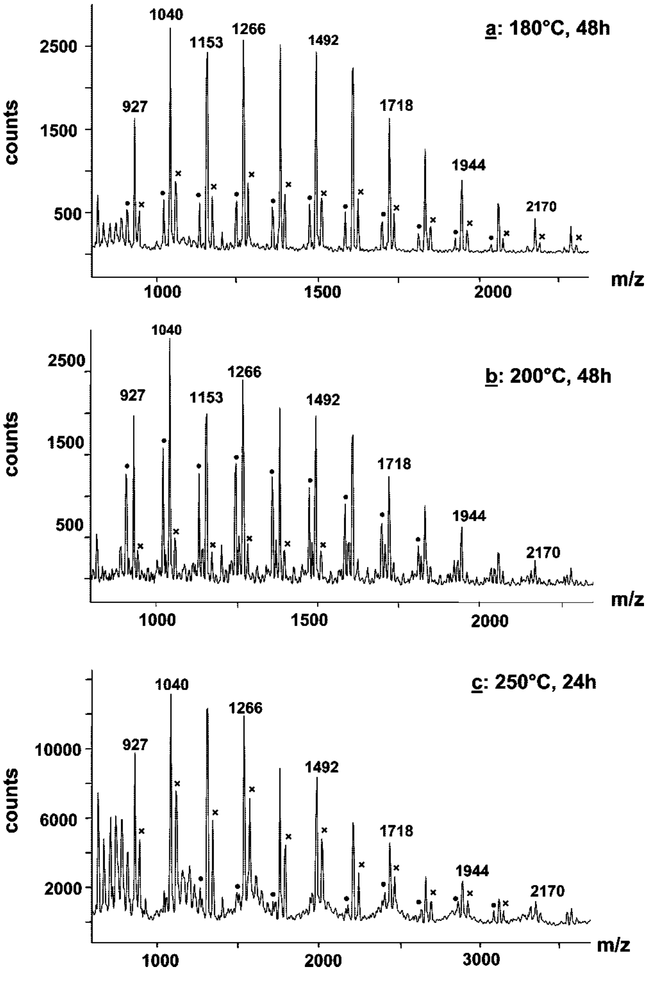
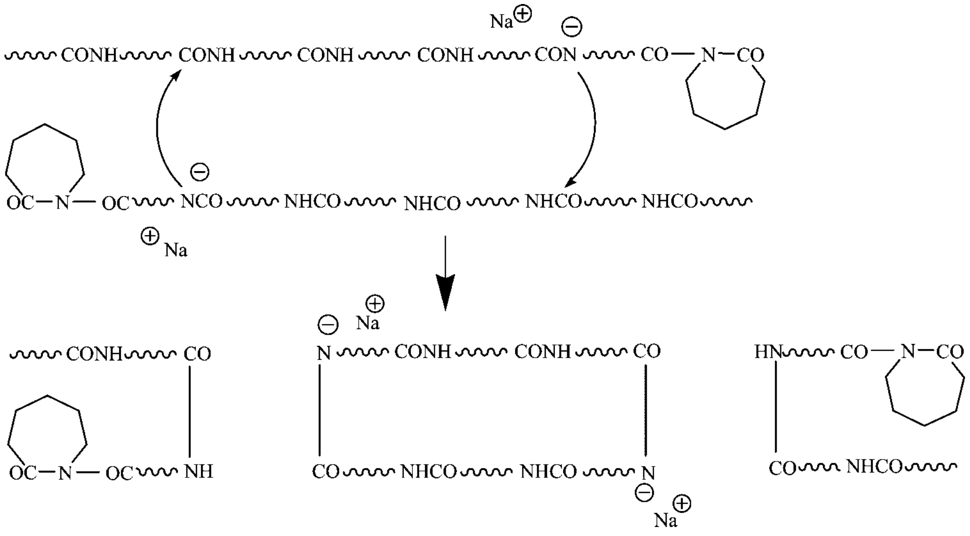


Figure 8. MALDI-TOF mass spectra of the sample F22 annealed at 180 (a), 200 (b), and 250 °C (c).

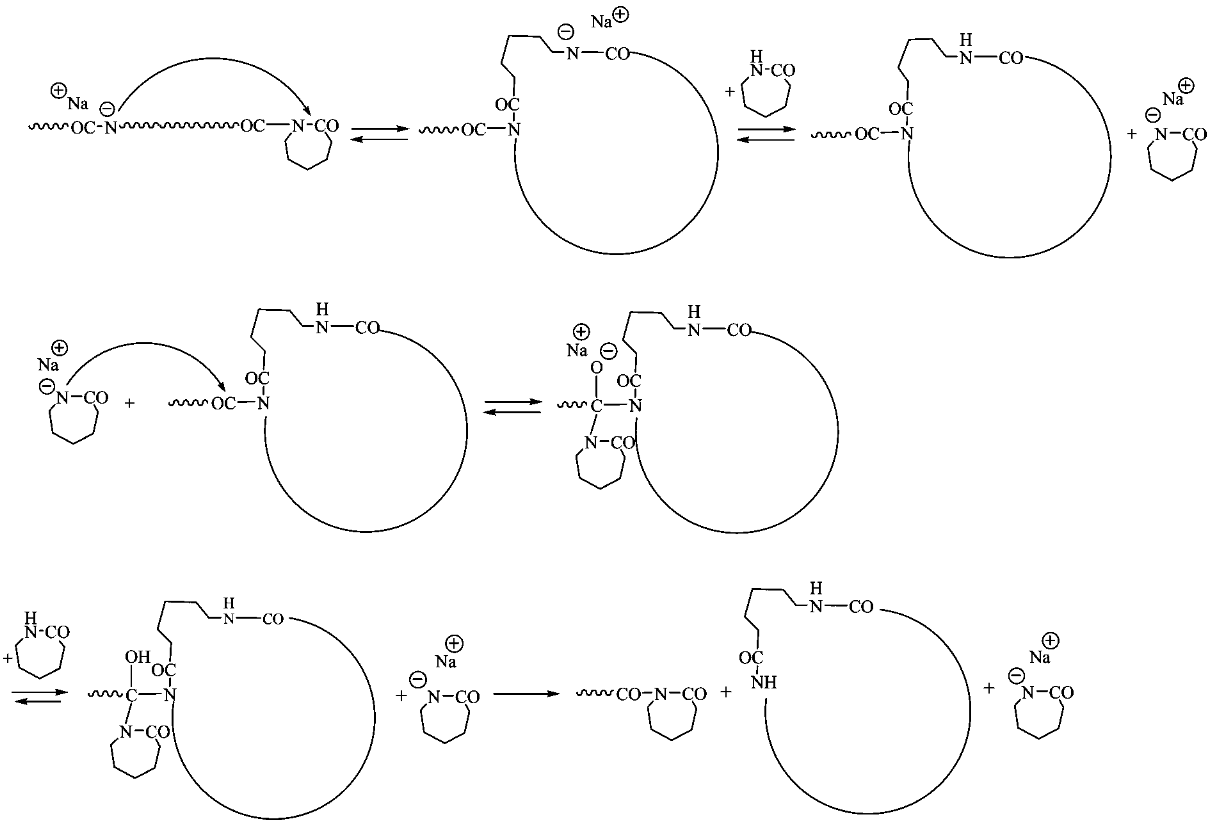
Conclusions

The GR peak typical of anionic PCL, identified in the first paper of this series as a macrocyclic *ensemble*, has been more deeply investigated in the present paper. A few reaction parameters, suitably chosen in order not to favor products of side reactions such as Claysen-type condensations, have been changed and the following conclusions can be drawn: (i) the GR peak, since the anionic polymerization of ε-caprolactam occurs in quasi-isothermal conditions, is not influenced by the polymerization method (suspension or bulk polymerization); (ii)

Scheme 1. Cycle Formation by Transamidation Reaction in Anionic Polymerization



Scheme 2. Cycle Formation by Backbiting in Anionic Polymerization



type and concentration of chain initiator, chosen among the ultrafast activators, are not responsible of the formation and the composition of GR peak; (iii) the content of macrocyclic PCL increases as the high polymer yield increases and the mechanism of its formation is very fast being already present, although in little amount, after 3 min only from the beginning of the polymerization.

Even though these conclusions are the result of investigations performed in a narrow range of modified parameters, they suggest that the mechanism of formation of macrocyclic species is independent of the mechanism of initiation of anionic polymerization and most probably involves polyamide growing chains with a rate very competitive to the propagation rate of CL anionic polymerization. In light of these considerations, the present work suggests a mechanism of macrocycle formation that seems more likely than the classical and slow transamidation reactions, which are at most responsible of cyclic oligomer formation in hydrolytic PCL. The proposal of a backbiting process to explain the presence of the high content of macrocyclic PCL is consistent with the both mechanism of anionic lactam polymerization and its side reactions and with the experimental data present here.

Furthermore, the attempt of bringing anionic PCL to thermodynamic equilibrium opened new questioning in the area of polyamide annealing and previous literature findings. Content and composition of GR peak in PCL annealed at different temperatures have been evaluated by MALDI mass spectrometric analysis, and no detectable difference with the "as-polymerized" reference sample has been found. The nonquantitative character of MALDI in the experimental conditions followed in the present work did not allow us to determine the exact content of individual macrocycles in annealed samples but has revealed that almost no change of their distribution occurred as a consequence of the thermal treatments. These results could suggest that the macrocyclic *ensemble* of anionic PCL is thermodynamically stable even though it is our opinion that further investigations are needed. A study exploring the possibility of longer thermal treatments without inducing any thermal degradation is in progress, with the aid of new chromatographic and spectrometric methods for quantitative evaluation of macrocyclic species.

The HPLC analysis of low molar mass cycles (M_1-M_7) in annealed PCL evidenced that the expected molecular reorganization does not occur in the solid state but only, and slowly, in the molten polymer. Also, the above behavior for low-mass oligomers deserves a deeper insight and is in progress in order to question or validate the data existing in the literature.[19]

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