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Nature of a Low Molar Mass Peak in Anionic Poly(ϵ-caprolactam). Its Identification as Macrocyclic Ensemble

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ABSTRACT: It has been found that anionic poly(ϵ-caprolactam) exhibits the peculiarity of a secondary SEC peak at intermediate elution times between the traces pertaining to the high polymer and those of the extracted oligomer fraction, irrespective of the conditions of synthesis, either nonisothermal (quasi-adiabatic) or isothermal. As yet, such a peak has never been evidenced in the literature. Synthesis in isothermal conditions at relatively low T allows to get rid af all structural irregularities, linked to nonisothermal anionic conditions, and analyze in depth the nature and extent of the above peak. Together with other characterization techniques, MALDI-TOF analysis has revealed that the peak is entirely composed of macrorings made of multiples of ϵ-caprolactam repetition unit, typically from M_9 to M_{19}, in amounts linked to the experimental conditions of the synthesis, but usually of ca. 2.5 wt %, as referred to the high polymer content. This amount is exceedly larger than the value extrapolated from the lower oligomer ($x \leq 8$) content and cannot be justified by any ring−chain thermodynamic equilibrium approach. On the other side, also for lower oligomers striking discrepancies exist between theory and experimental results. A general overview, including also cyclic oligomer content in hydrolytic poly(ϵ-caprolactam) samples, is provided, and a critical analysis of the extraction methods described so far in the literature is given.

Introduction

The formation of cyclic oligomers (M_x) in the ring-opening polymerization of ϵ-caprolactam (CL) by either hydrolytic or anionic route, as well as their relative content in poly(ϵ-caprolactam) (PCL), plays a relevant (mostly negative) role on properties and performances of the above polyamide. Typically, extensive extractions with suitable solvents are needed in industry in order to remove M_x and other low molar mass species prior to any PCL utilization in both plastics and fiber production, with the notable exception of cast nylon and RIM technologies.

In general, a sizable formation of low molar mass cyclic species besides linear chains is almost invariably present in step-growth and ring-opening polymerizations, where also a relevant portion of high molar mass products may consist of rings, as suggested by Kricheldorf et al.[1] The whole extractable fraction obtained by washing solid PCL by hot methanol or boiling water (most used extraction media) amounts to 11−12 wt % for hydrolytic PCL,[2−4] with 7−8% of residual CL and 3−4% of higher cyclic oligomers, while linear oligomers represent a very small fraction of the polymerization products (less than 0.2% in total).[3] In the activated anionic polymerization of ϵ-caprolactam the residual monomer content is considerably lower, as compared to the hydrolytic route, and the higher cyclic oligomers are found to be in smaller amounts, too,[2,5−7] being the whole extractable fraction usually in the range of 2−3 wt %, depending on process parameters. It is worth mentioning here that for samples of PCL, obtained after prolonged annealing at 180 °C, the relative composition of each cyclic oligomer is reported to be almost the same for both hydrolytic and anionic materials,[2,3] as a claimed proof of the attainment of ring−chain equilibria, independently of the polymerization mechanism. Later on, we will see that a reexamination of the above results is suggested by the present paper.

The chemistry and mechanism of anionic ring-opening polymerization of lactams have been studied quite extensively since the 1970s, especially by Šebenda et al.[8−11] and Sekiguchi et al.,[12] although a comprehensive pattern of this polymerization has never been fully and unequivocally clarified, mainly because of the simultaneous presence of complex side reactions derived from both the strong basicity of the medium and the relatively high polymerization temperatures, leading to extensive PCL branching or even cross-linking and many structural irregularities, besides the formation of several low mass side products. Even a small variation of process parameters (temperatures and times of polymerization, nature and concentration of active species, and so on) can consistently affect chemistry and kinetics of the reaction, leading to a wide range of products with different relative contents.

Following some previous studies on activated anionic polymerization of ϵ-caprolactam,[13−15] more recent findings of our research group[16,17] have shown that, if the anionic polymerization is carried out in isothermal conditions at relatively low temperatures (ca. 150 °C) and by very fast activators (chain initiators), PCL in very high yields and free of structural defects and side products is produced. Moreover, in these conditions higher molar masses of PCL and narrower polydispersities can be achieved (typical values are in the range of $M_w = 50$K g/mol and $D = 1.8$ by the SEC-MALS technique).[18] Isothermal conditions can, therefore, allow to evaluate the two polymerization products, linear chains and rings, more accurately and in more detail, without the interference of side reactions which badly affect anionic processes in quasi-adiabatic conditions.

An accurate evaluation of high polymer molar mass distribution and cyclic oligomer content in isothermally produced anionic PCL is relevant in this respect. Therefore, a thorough

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analytical work by SEC and HPLC has been accomplished on relatively large amounts of laboratory-made polymerization products. All anionic PCL syntheses have been performed in isothermal conditions, as mentioned above, by both bulk and suspension polymerization approaches, following recipes described in detail in refs 16 and 17. SEC analytical methods on the high polymer fraction have been extensively described in ref 18 for some typical anionic samples. At that time, a peculiar feature present in all samples has been noticed and has prompted us to carry out further, more detailed studies, which will be shown in the present work together with some considerations on the evaluation of the content of cyclic oligomers ($x \leq 8$), as determined by the extraction procedures used so far.

Let us start with the first aspect. In the SEC chromatograms, all anionic poly(ϵ-caprolactam) samples have evidenced the sizable presence of low molar mass species as a well separated peak, from now on coded GR peak, present at intermediate elution times as compared to those of the high polymer peak and of the extractable cyclic oligomers, whose content quickly decreases from dimer to hexamer, as commonly quoted in the literature.[2,5] Indeed, all literature reports given so far on anionic PCL have never revealed the presence of GR peak, being typically limited to the evaluation of the content of extractable cyclics from dimer to hexamer, very seldom to nonamer, and being SEC analyses of PCL very difficult to realize in practice.[18] Coming to the second point, which will be now introduced in more detail, it can be underlined that the regular decrease of M_x content as a function of its size, irrespective of the reaction mechanism, either hydrolytic or anionic, has been quite often compared in the literature to the values predicted by thermodynamic theories, namely the Jacobson−Stockmeyer approach,[19] which can obviously be applied only to equilibrium conditions.

Let us now discuss in detail the state-of-the-art on ring−chain equilibria. Indeed, these equilibria in polymer systems have been studied since 1950, when Jacobson and Stockmayer[19] developed an elegant theory of cyclization. Their theory provided a theoretical expression for concentrations of ring molecules in equilibrated condensation polymers having chains of sufficient length to obey Gaussian statistics and assuming equal reactivities of the sites, strainless rings, negligible end-group effect, and thermodynamic equilibrium between M_x rings and chain molecules:

$$-M_y- \Delta -M_{y-x}- + M_x \tag{1}$$

Under the above conditions, the equilibrium between x-meric cyclics and linear polymer chains is not affected by the nature of terminal groups in the linear chain; therefore, these latter do not enter into any theoretical consideration related to equilibrium cycle concentration. Macrocyclization equilibria (1) are able to describe the behavior of linear polymer chains, when these are allowed to reach thermodynamic equilibrium and generate cyclic oligomers. Consequently, in this process also depolymerization of a high molar mass linear chain can be involved in an analogous manner, and the formation of cyclic oligomers can be considered the result of an intramolecular reaction. Of course, the equilibrium is assumed to be independent of the specific polymerization mechanism.[2,3] Excellent reviews on the subject have been published.[20,21]

The Jacobson−Stockmayer theory has been applied to PCL using the RIS model of Flory and Williams,[22] and the content and composition of cyclics have been calculated.[20,23−25] Namely, the molar cyclization equilibrium constant K_x for the x-meric ring molecule M_x has been evaluated and compared to experimental data. Discrepancies between calculated equilibrium data and experimental values for cyclic oligomers of PCL have been reported, resulting in experimental K_x values somehow lower than the theoretical ones calculated by the Jacobson−Stockmayer theory.[2,3,20,23,24] For instance, hydrolytic PCL has been predicted to contain from 5 to 8 wt % of cyclics with $x \geq 6$,[23] whereas the experimental values reported for hydrolytic PCL give values lower than 1%.[2,4,23] Strong discrepancies also on monomer content have been found and have been attributed by Wichterle et al.[26,27] and, later on, by Reimschuessel[28] to the role of crystalline regions and, in general, of the structure and morphology of PCL on ring−chain equilibria. In our opinion, first of all, any comparison of our system with other systems under thermodynamic equilibrium control[29−31] should be ruled out, being our fast anionic processes kinetically, not thermodynamically, driven. Furthermore, it has to be stated here that the theoretical prediction for cyclic concentrations did not match the experimental values, even for equilibrated PCL samples, inasmuch as these results were always obtained from oligomer extraction by boiling water or methanol. Indeed, it is relevant to point out that it has been recently found[32] that the oligomer extraction technique by boiling water or hot methanol is not at all able to remove the whole oligomer fraction. The careful analytical study quoted above on the evaluation of cyclic oligomer content in PCL reveals the poor extraction efficiency by such methods and shows that only the cyclic monomer, dimer, and trimer are fully extracted. Tetramer extraction is not complete, and from pentamer to nonamer the solubility is lower and lower in the extracting solvents. This is a very important aspect since the extraction by methanol or water is the most widely used method to separate the cyclic oligomers from the high polymer, and all studies and theoretical models present so far in the literature have been based on the assumption that experimental data obtained by such technique are representative of the true oligomer content. On the basis of the above work,[32] it is now quite reasonable to assert that the real concentration of higher oligomers ($x \geq 4$) largely exceeds the amounts usually considered in literature and that all previous studies on ring−chain data for PCL have to be ruled out.

In the present study, besides a full extraction of M_x species from monomer to nonamer by a new fractionation technique, we have developed a procedure in order to properly evaluate also the content and the nature of the low mass species (GR peak) present in PCL. A full analytical characterization of this low mass fraction has been accomplished, and the identification of its chemical nature has been achieved.

Experimental Section

Synthesis of Polyamide 6. Polyamide 6 samples were laboratory preparations synthesized by activated anionic polymerization of CL, as follows:

Quasi-Isothermal Suspension Polymerization. Low molar mass polyisobutene (PIB) was the suspending medium, while sodium caprolactamate (NaCL) was the polymerization initiator and cyclohexyl carbamoyl caprolactam (CCCL) was chosen as ultrafast activator. A powdered product was obtained. The experimental parameters for the synthesis were the following: polymerization temperature, 155 °C; polymerization time, 10 min; NaCL concentration, 0.6% (mol/mol of CL); CCCL concentation, 0.6% (mol/mol of CL). Additional experimental details have been published elsewhere.[17]

Isothermal Bulk Polymerization. Polymerization reactions have been carried out in a stainless steel mold with a disk-shaped die (thickness 0.8 mm) ensuring a fast dissipation of polymerization heat. NaCL was the initiator and CCCL the activator. The experimental parameters for the synthesis were the same as for the suspension process. More details are given elsewhere.[16]

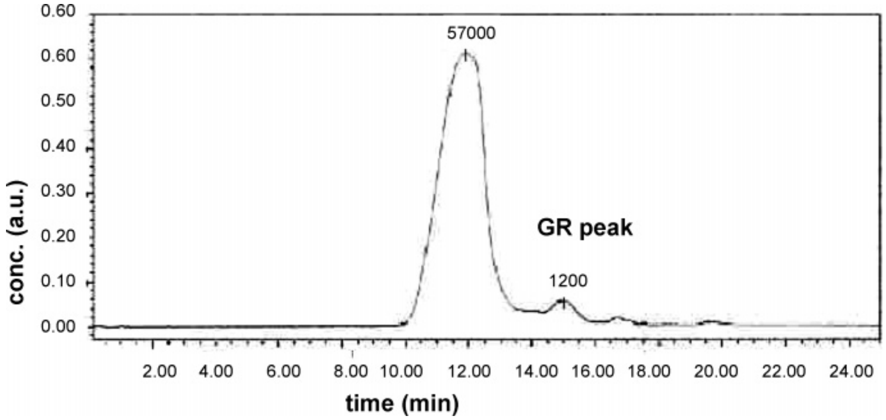

Figure 1. SEC trace of anionic PCL (sample LR9) synthesized by suspension polymerization and extracted with methanol.

Polyamide 6 Fractionation. ϵ-Caprolactam and higher cyclic oligomers were preliminarily, although not completely, separated from both the species forming the GR peak and the high polymer by Soxhlet extraction with methanol for 8 h. Then, methanol was removed from the solution by rotovapor. Subsequently, GR peak species were separated from the high polymer by a selective precipitation, as follows: 0.4 g of sample, previously washed with methanol, were dissolved in 40 mL of 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP). Then, methanol (66 mL) was slowly added to this solution under stirring, and after 2 h the precipitate was filtered. The clear solution was dried by solvent removal in rotovapor, and the powdered species belonging to GR peak were characterized.

Measurements. Size exclusion chromatography (SEC) and high-performance liquid chromatography (HPLC) analyses were carried out with the same instrumentation: 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).

SEC analysis of the high polymer fraction was carried out in HFIP containing 0.01 M tetraethylammonium nitrate (TEAN) (sample concentration 2 mg/mL) at 35 °C with a flow rate of 0.5 mL/min. PDA, selected at a wavelength of 215 nm, and RID were 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 (relative calibration curve). Size exclusion chromatography of GR peak was performed in a 30/70 v/v mixture of HFIP and CH_2Cl_2. Sample concentration was 2 mg/mL; the column heater was kept at 30 °C and flow rate at 1 mL/min. Four Ultrastyragel columns (7.8 × 300 mm) were used in this respect, and the refractive index detector was preferred to photodiode array detector. Also in this case, relative molar masses were evaluated with reference to poly(methyl methacrylate) (PMMA) standards. High-performance liquid chromatography runs were performed following a method published by Guaita[33] with a few modifications. Eluent: a 40/60 volume 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 selected at 210 nm. Two calibration curves were calculated by using CL and its cyclic dimer as external standards. Moreover, the samples for this analysis were prepared by selective precipitation as described above, but without previous Soxhlet extraction with methanol.

^1H NMR spectra (D_2SO_4) and ^{13}C NMR (TFE/$CDCl_3$) were recorded on a Varian model Gemini 200 MHz. FT-IR spectra in KBr were recorded on a Bruker model IFS66.

Differential scanning calorimetry was performed on a Mettler calorimeter model TC 10A with a speed rate of 10 °C/min.

MALDI Mass Spectrometric Analysis. MALDI-TOF mass spectra were acquired on a Voyager DE-STR (Applied Biosystems, Foster City, CA) with delayed extraction (20 kV applied after 233 ns with a potential gradient of 2545 V/mm) and detection in reflection mode. The instrument was equipped with a nitrogen laser (emission at 337 nm for 3 ns) and a flash AD converter (time base 2 ns). Each MALDI experiment was performed by loading about 0.1 mmol of sample and 40 mmol of *trans*-3-indoleacrylic acid (IAA, used as a matrix) on the sample plate, using THF as a solvent. The mass calibration was performed as reported in previous cases.[34]

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 in 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

As the first step, the SEC method to fully separate high polymer from low molar mass species has been studied and optimized. According to a previous publication of our group,[18] HFIP solvent has been chosen as mobile phase and TEAN added in order to effectively eliminate early elution of the polymer in HFIP as well as gel formation. In the present need, three Zorbax silanized silica columns have shown to be efficient and, as regard to the detector, RID and PDA (selected at 215 nm) gave good traces, with the only difference that, when RID is considered, the signal of the mobile phase hides the peaks corresponding to the lowest molar mass species (i.e., CL, dimer, and a few other oligomers). Figure 1 shows a sample of anionic PCL, synthesized by suspension polymerization (sample LR9),[17] only washed with hot methanol: the trace, recorded using PDA, allows an easy identification of three characteristic areas. At low elution times the high polymer curve ($M_p = 57\,000$) is present, followed by a well-separated peak, linked to relatively low molar mass species and centered on a molar mass of about 1200 g/mol. Finally, at higher elution times, small amounts of cyclic oligomers down to ϵ-caprolactam can be noticed, as further confirmation of literature findings[32] that methanol extraction is not fully effective in the removal of these species, especially for masses higher than cyclic tetramer. Moreover, it should be remarked that the value of peak molar mass for the high polymer, although only calibrated with PMMA standards, is not far from the value calculated for the same sample by viscometric analysis ($M_v = 48\,000$) and previously published.[17]

On the basis of this agreement, we can assume that 1200 is a possible starting value for the average molar mass of the low molar mass species forming the GR peak, provided that the same relative calibration with PMMA samples holds also in this low molar mass region.

Also, a sample of anionic PCL (sample F22),[16] synthesized by isothermal mass polymerization, has been analyzed by SEC

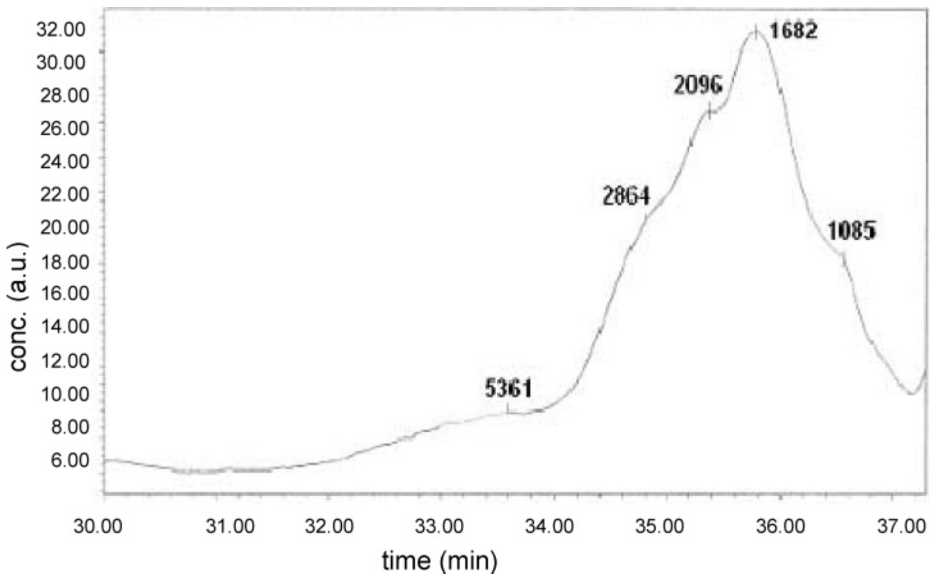

Figure 2. SEC trace of low molar mass species (GR peak) of the sample LR9 (anionic PCL synthesized by suspension polymerization method).

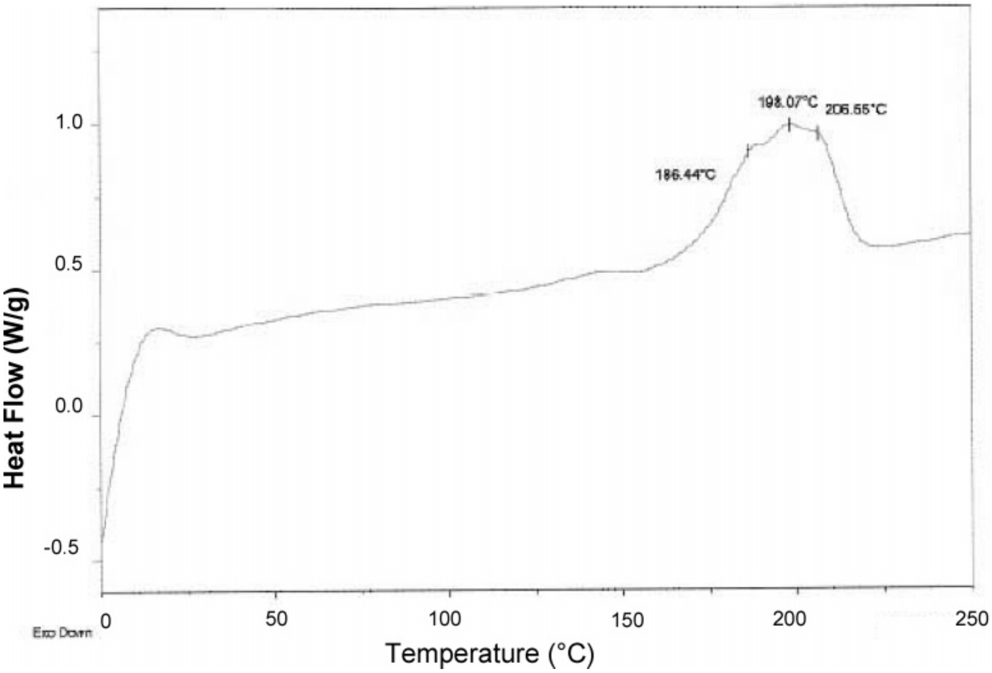

Figure 3. DSC of GR peak species of the sample LR9.

chromatography and its trace (not given) compared to the previous one. The aim of this comparison was to investigate whether suspension and bulk polymerization, being both isothermal syntheses carried out using the same experimental parameters, can provide the same results in terms of PCL molar mass and molar mass distribution. Moreover, we were aimed to verify the presence and extent of low molar mass species forming GR peak when different polymerization techniques are used. We found that the SEC traces are fully superimposable.

For the sake of comparison, a commercial PCL (polymerized by hydrolytic mechanism and kindly supplied by Radicifil S.p.A.) has been analyzed following the same chromatographic method. From the SEC trace (not given) it can be noticed that hydrolytic PCL is characterized not only by a relatively lower molar mass and higher polydispersity but also by the absence of the GR peak, as found in the anionic samples. Typically, a large step instead of the peak follows the lower mass side of the high polymer peak until the baseline is fully restored. In a future work its nature will be described and compared to that of the anionic sample.

Subsequently, the SEC method was modified by changing a few parameters, as described in the Experimental Section, in order to focus our investigation on the nature of low molar mass species grouped as the GR peak. Figure 2 shows the SEC trace of the same sample LR9 after extraction with methanol followed by its separation from the high polymer. The multimodal chromatogram reveals that the peak, observed in Figure 1 as a single peak, is here well resolved and corresponds to a mixture of different molecules characterized by several peak molar masses, whose values (relative to PMMA calibrations) are given in the same figure.

Corresponding results were obtained by heating the same sample in a differential scanning calorimeter up to melting. The

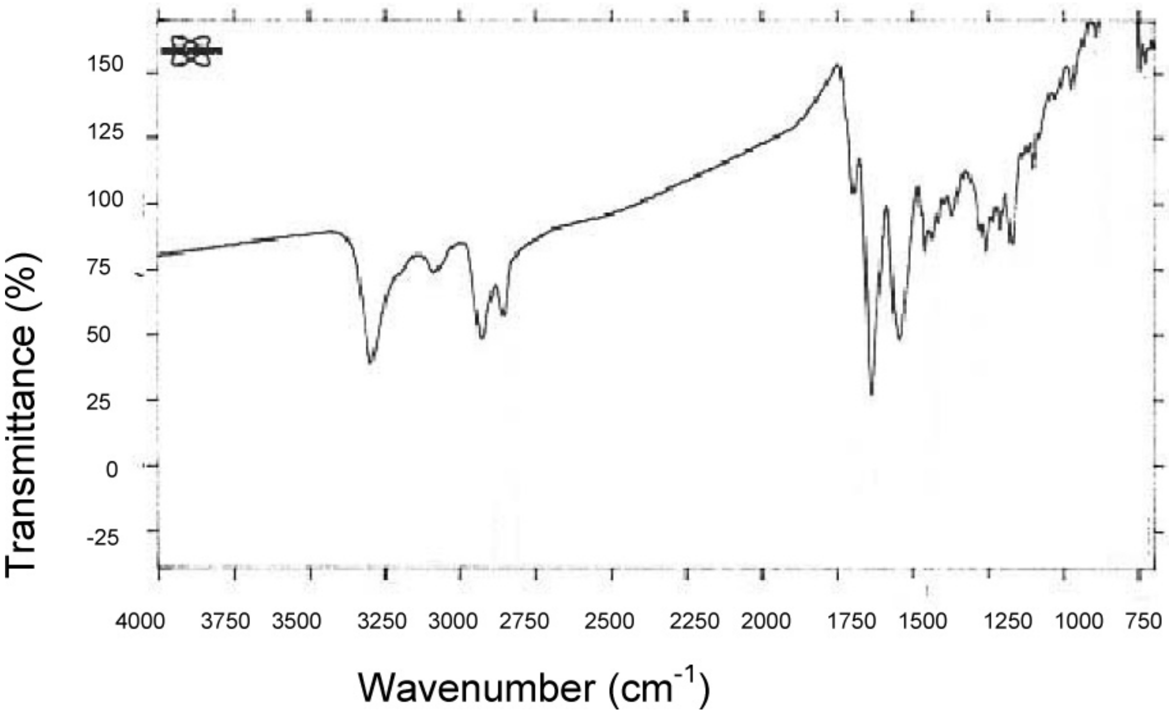

Figure 4. FT-IR of GR peak species of the sample LR9.

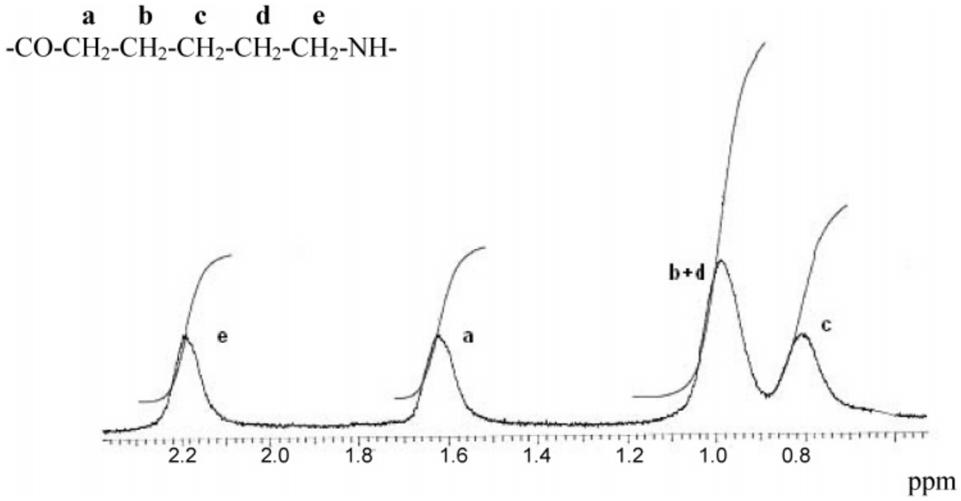

Figure 5. ^{1}H NMR of GR peak species of the sample LR9.

DSC multimodal trace (Figure 3) shows the presence of species melting at different, albeit very near temperatures, starting from 170 °C and ending at about 210 °C. This experimental evidence may suggest a close similarity in the molecular structure of the above species which, in agreement with SEC data, present only a difference in molar mass.

These molecules have been further analyzed by FT-IR spectroscopy, as shown in Figure 4, and only the typical signals of polyamide 6[35] were observed. The appearance of a strong band at 3297 cm^{-1} is attributed to the NH stretch of the amide groups; CH$_2$ stretch peaks are at ca. 2930 and 2860 cm^{-1}, while C═O bond stretching gives a strong signal at 1640 cm^{-1}. Other two signals at 1540 cm^{-1} (C−N stretch + CO−NH bend) and 3090 cm^{-1} (its overtone) are characteristics of amide groups. The identification of a PCL-like structure is confirmed by other peaks at 1371 cm^{-1} (w, CH$_2$), 1261 cm^{-1} (w, CH$_2$), 1200 cm^{-1} (w, CH$_2$), and 1120 cm^{-1} (w, CC) and by the absence of spurious signals.

^{1}H NMR spectroscopy of the GR peak performed in D$_2$SO$_4$, as evidenced in Figure 5, gave a spectrum characterized by four signals at low ppm (at 0.8, 1, 1.6, and 2.2). Also in this case, the comparison with a PCL reference spectrum[35] allowed us to attribute the signals, without any doubt, to a PCL-like structure being the signals in the typical position of the five methylene groups of the PCL repeat unit.

^{13}C NMR has been performed in TFE/CDCl$_3$, as published by Davis et al.,[36] being sulfuric acid inadequate for long time analysis. The ^{13}C NMR spectrum confirmed the conclusions drawn by ^{1}H NMR analysis: as evidenced in Figure 6, the spectrum is composed of six peaks at the characteristic shifts of the six carbons of PLC.[35,36]

The above part of our work gave us the assurance that the low molar mass species forming GR peak are molecules composed of PCL repetition units only and by different molar masses close to multiples of 113.16, which corresponds to the mass of CL repetition unit. The possibility that these species

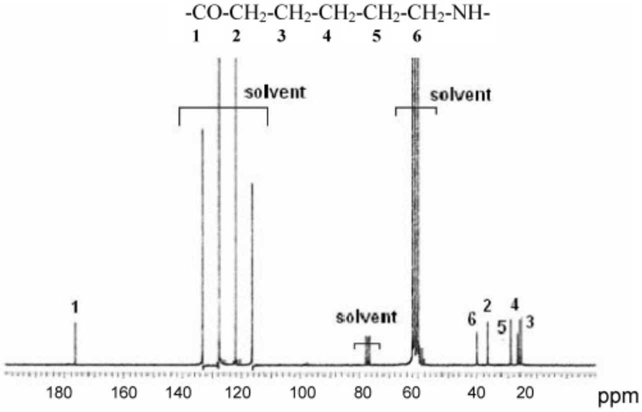

Figure 6. ^{13}C NMR of GR peak species of the sample LR9.

are PCL cyclic oligomers with molar masses distintly higher than those of the cyclic oligomers extracted by methanol has been proved by MALDI-TOF mass spectroscopy, as shown below, i.e., by a technique able also to determine the presence and the nature of end groups.

The positive MALDI-TOF mass spectrum of low molar mass species is reported in Figure 7. The experimental values of *m*/*z* have been compared with the theoretical values of molecules constituted of the general formula

$$X-(CO-CH_2-CH_2-CH_2-CH_2-CH_2-NH)_n-Y$$

where X and Y are all possible end groups that the anionic mechanism of CL polymerization can generate.

Indeed, the spectrum essentially consists of a series of intense peaks at *m*/*z* values n113 + 23 corresponding to sodiated ions of cyclic oligomers of PCL from hexamer (peak at *m*/*z* 701) up to nonadecamer (at *m*/*z* 2170). Peaks due to species with higher molar mass are also present with very low intensity, and the peaks indicated in the spectrum as # (at *m*/*z* values n113 + 39) are also due to cyclic oligomers detected as potassiated species.

The above calculations have shown the complete absence of end groups, thus demonstrating that only cyclic oligomers of PCL are present, with a mass from 679 (hexamer) up to 2150 g/mol (19 repetition units). Also in this case, somehow confirming the relative data obtained by SEC chromatography (Figures 1 and 2), the maximum of their population is pointed on the value of 1020 g/mol (cyclic nonamer). Traces of lower cyclic oligomers have been detected also by this analytical method, once more underlining the incompleteness of the usual extraction processes.

Table 1. Cyclic Oligomer Content, c[M$_x$], in LR9 Not Previously Washed in Methanol

x	M_x (wt %)	M_x (mol/100 mol of PCL repeat units)
1	1.51	1.515
2	0.40	0.200
3	0.13	0.042
4	0.09	0.023
5	0.08	0.017
6	0.11	0.018
7	0.11	0.016
8	0.19	0.023
9	0.27	0.030
10	0.09	0.009
11	0.09	0.008

A quantitative evaluation of low molar mass species (GR peak), which we can now call PCL macrocyclics, has been performed by HPLC, using the classical method already employed for the lower cyclic oligomers.[33] In particular, we have analyzed a sample composed of PCL macrocycles and the whole content of lower oligomers. For this purpose, a sample has been prepared as described in the Experimental Section, without any previous extraction with methanol. Evaluation of cyclic and macrocyclic oligomer content in anionic PCL on unwashed LR9 is given in Table 1, where M_x from CL to M_{11} are present. The values listed, in terms of molar as well as weight concentration, confirm the information obtained from SEC and MALDI analysis on the trend of GR peak (maximum concentration for M_9) and give reliable information about the distribution of lower cyclics. Namely, when oligomers from CL to pentamer are considered, a regularly decreasing trend as a function of molar mass is observed, followed, from M_6 on, by an increase up to a maximum corresponding to M_9. By the HPLC method, a very low content of M_{10} and M_{11} has been detected, most probably because of a strong retention by the column used. Moreover, this method does not allow the detection of macrocyclics higher than M_{11} because they are not soluble in the HPLC eluent (TFE/H_2O = 40/60 vol). A suitable SEC method

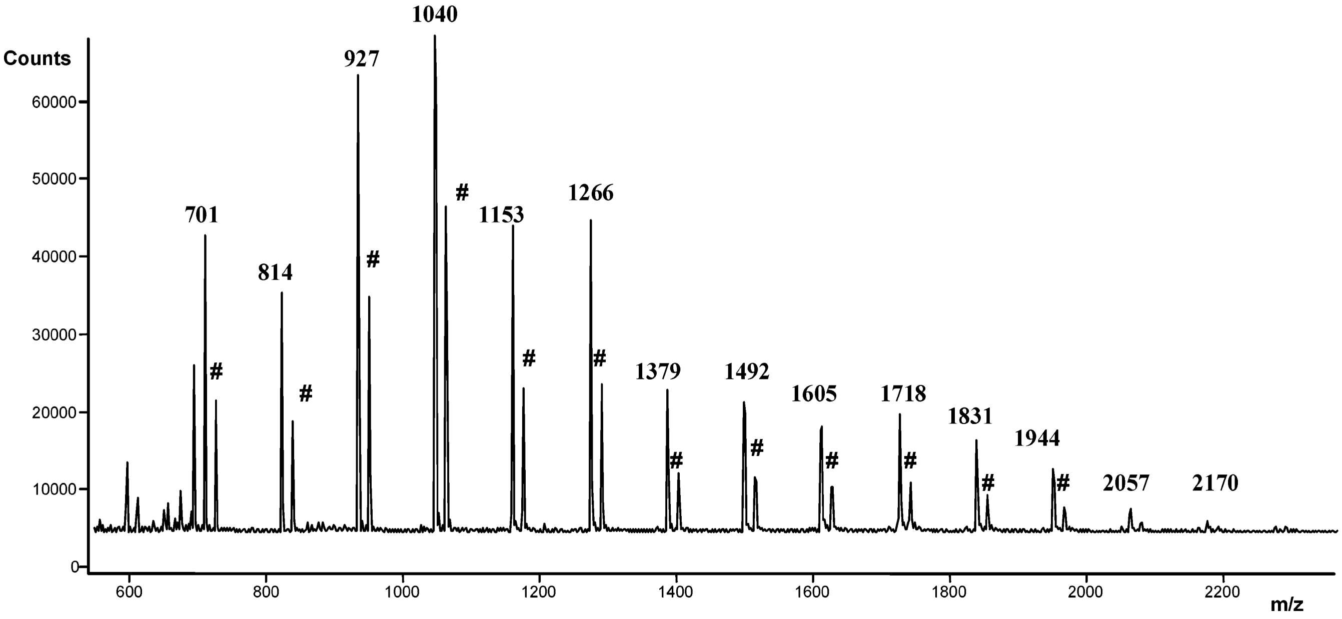

Figure 7. MALDI-TOF of GR peak species of the sample LR9.

to analyze $M_x > M_{11}$ is in progress and will be published elsewhere.

Conclusion

On the basis of the results shown above, we can draw the following conclusions: a previously undiscovered peak (GR peak), always present in anionic PCL samples, has been found by SEC and HPLC analyses. The peak, situated between the high polymer trace and the cyclic oligomer fraction, is made of macrocycles only (as evidenced by MALDI-TOF), usually ranging from the nonamer up to M_{25} as functions of the experimental conditions of anionic synthesis. Its constituents are not at all extracted from PCL by the usual extraction techniques, and their overall concentraton is in the range of a few percent (2−3 wt %), i.e., a much higher concentration than the values attributed in the literature to the higher oligomer fraction.

Furthermore, on the basis of the present results, we can conclude that previous literature data, based on water- or methanol-extractables, are misleading as they provide only a partial contribution to the total content of each cycle up to $x = 9$. If one takes in account the latter values, once more it is found that Jacobson−Stockmayer theory does not apply to anionic PCL, whose formation, as said above, is under kinetic, not thermodynamic, control. In the next paper of the series, some deeper insight into the formation of GR peak as a function of experimental parameters will be given. Possible mechanisms of its formation will also be put forward. An attempt to study the nature of the step in hydrolytic PCL, whose SEC trace more or less corresponds to GR peak in anionic samples, will also be presented in the same paper.

In the present work we have confirmed what was reported in ref 32; i.e., hot methanol/boiling water extraction is not able to remove to whole amount of cyclic PCL oligomers, from tetramer on, from either anionic or hydrolytic polyamide samples. Therefore, also from the latter ones, even for ring−chain equilibrates, experimental values of molar cyclization equilibrium constants K_x, given so far in the literature,[20,23,24] are biased by deficient extraction procedures and cannot be correctly compared to Jacobson−Stockmayer theoretical values.

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