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Determination of the residual monomer concentration of ε-caprolactam in polyamide-6 using thermogravimetric analysis coupled with Fourier transform infrared spectroscopy gas analysis

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Abstract

For the anionic polymerization of ε-caprolactam to polyamide-6 the residual monomer concentration in the final polymer is an important characteristic. To determine this residual ε-caprolactam monomer concentration, a fast and fail-safe method was developed, which couples thermogravimetric analysis (TGA) with Fourier transform infrared spectroscopy (FTIR) gas analysis. FTIR allows an identification of the types of gasses released during heat treatment. Calibration of the infrared absorbance of ε-caprolactam and the corresponding mass loss in TGA allows a quantitative evaluation of the ε-caprolactam monomer release. Low-heating rates and powdery samples guarantee high-precision measurements.

KEYWORDS

polyamides, ring-opening polymerization, spectroscopy, thermogravimetric analysis, thermoplastics

1 | INTRODUCTION

Polyamide-6 is a cost-efficient engineering thermoplastic, which is widely used as pure polymer or as polymeric matrix in composite materials in combination with carbon or glass fibers. Polyamide-6 is a semicrystalline polymer, which has sufficient mechanical properties for many applications, chemical resistance, and recyclability.[1–6]

There are three different reaction routes used to produce polyamide-6, namely hydrolytic, cationic, and anionic polymerization of ε-caprolactam, which differ mainly in the initiation of the polymerization reaction.

The cationic polymerization of ε-caprolactam is initiated by acids and is rarely used, since it yields low-molecular weight products at low conversions.[7]

Most frequently, polyamide-6 is produced by hydrolytic polymerization of ε-caprolactam. The water-induced polymerization is characterized by two reaction steps: (1) ring opening of ε-caprolactam by hydrolysis, which results in ε-aminocaproic acid and (2) chain growth. Chain growth can happen in two different ways: (2a) addition of ε-caprolactam to the aminogroup of ε-aminocaproic acid under ring opening and further stepwise addition of ε-caprolactam units to the amino group of the growing polymer chain under ring opening, and (2b) condensation reactions between amine and carboxyl

groups of ε-aminocaproic acid with formation of amide groups and water molecules.[8–11] Step 2a represents the main chain growth reaction, while step 2b is of minor importance.[10] The polymerization temperature is above the melting temperature of polyamide-6 of 221°C[12] and the polymerization reaction takes several hours.[8,9,11] The final product still contains on average 8–9 wt% of monomer molecules and about 3 wt% of low-molecular weight, mostly cyclic oligomers. Their removal is performed either by hot water extraction or by vacuum evaporation.[9]

In the anionic polymerization of ε-caprolactam to polyamide-6 strong bases, such as alkali metals, work as so-called initiators or catalysts and form free ε-caprolactam anions. Often sodium caprolactam or magnesium bromide caprolactam are used for the initiation.[7] A nucleophilic attack of the ε-caprolactam anion on a ε-caprolactam monomer takes place, which by fast proton exchange results in a new ε-caprolactam anion and aminoacyllactam. Chain growth takes place by repeated nucleophilic attack of the ε-caprolactam anion on the endocyclic carbonyl group of the non-ionic growth center, that is, the N-acylated terminal lactam ring.[7,9,10] The ε-caprolactam anion is reproduced after each growth step.[9,10,13,14] As the formation of N-acylated lactam is the controlling step of the anionic polymerization, the propagation rate can be enhanced by the introduction or in situ generation of N-acyllactam structures, which act as additional growth centers. Such N-acyllactam structures, for example, hexamethylene-1,6-dicarbamoylcaprolactam, are called activators.[7] The anionic polymerization of ε-caprolactam to polyamide-6, which was first patented in 1941,[15] is characterized by short reaction times of a few minutes, conversions up to 99 wt%, low-reaction temperatures below the melting point of polyamide-6,[1,16–19] and improved polymer properties, for example, a higher crystallinity and high-molecular weights up to 10^6 g/mol compared to hydrolytic polymerization.[1] In particular, the low-residual monomer concentration of the order of 1 wt% represents an advantage compared to hydrolytic polymerization.

The described process parameters of the anionic polymerization and the extremely low viscosity of ε-caprolactam (5 mPa·s at 100°C[20]) are advantageous for the production of fiber-reinforced polyamide-6. In the so-called in situ polymerization process, a fiber semi-finished product is infiltrated by the reactive mixture of ε-caprolactam, activator, and initiator, which then polymerizes in a few minutes at temperatures between 130 and 170°C to polyamide-6.[19]

The degree of conversion or, correspondingly, the residual monomer concentration is an important property of the polymerization reaction of the initial monomer units to polymer molecules. It directly influences the mechanical properties of the polymer. To determine the residual monomer concentration in polyamide-6 several methods exist, which are compared in ref.21.

One technique is gravimetry after solvent extraction of the monomer. After grinding, the polymer is treated for several hours in a solvent, commonly methanol[13,22,23] or distilled water,[1,24,25] which dissolves the low-molecular weight monomer molecules from the polymer. The residual monomer concentration is determined by the weight ratio of the dissolved monomer and the polymer before extraction. Also gravimetry after vacuum drying is performed, where the residual monomer concentration is removed from the polymer by vacuum and elevated temperatures.[21] Further methods to determine the residual monomer concentration are gas chromatography[26,27] and infrared spectroscopy.[28] Another qualitative method for determining the residual monomer and other oligomers within polyamide-6 is provided by the direct analysis in real time mass spectrometry (DART-MS) technique.[29–31]

A powerful method to determine the residual monomer concentration of polyamide-6 is thermogravimetric analysis (TGA) of the polymer under inert atmosphere.[21] The low-molecular weight residual ε-caprolactam molecules escape from the polymer in the temperature range between 100 and 200°C, while the high-molecular weight polyamide-6 polymer molecules start to decompose only at temperatures above 200°C.[32] Here, a depolymerization of polyamide-6 to ε-caprolactam takes place,[33] which is driven by intramolecular endgroup cyclization (end-biting) and cyclization within the polymer main chain (back-biting).[32] The depolymerization to ε-caprolactam can cause an overestimation of the residual monomer concentration. Larger cyclic oligomers are formed during thermal decomposition at temperatures above 390°C.[34]

This work presents an advancement of TGA of the residual ε-caprolactam monomer concentration in polyamide-6. Fourier transform infrared spectroscopy (FTIR) gas analysis was coupled with TGA, to identify the types of gasses released during thermogravimetric (TG) heat treatment as function of temperature. In this way, the starting temperature of the polyamide-6 depolymerization to ε-caprolactam can be identified. Correspondingly, the temperature range of release of residual caprolactam is well defined. A correlation of the FTIR absorbance of ε-caprolactam and the corresponding mass loss rate in TGA allows a quantitative, precise, and fast evaluation of the residual monomer concentration in polyamide-6.

2 | EXPERIMENTAL

2.1 | Materials

A polyamide-6 plate was supplied by Brüggemann GmbH & Co. KG based on the precursor materials AP-Nylon Caprolactam flakes (ε-caprolactam), initiator C10

(sodium caprolactam), and activator C20 (N,N′-hexane-1,6-diylbis[hexahydro-2-oxo-1H-azepine-1-carboxamide]). A mixing ratio of 98 wt% caprolactam, 1.2 wt% C10 and 0.8 wt% C20 was used. The reactive mixture was injected into a preheated mold at 160°C and held for about 5 min, where it was finally converted to polyamide-6. The resulting polyamide-6 plate has dimensions of 270 x 190 x 3.8 mm^3.

Different sample forms were prepared from the center of the plate, to investigate the influence of the sample geometry on the analysis results. Using a low-speed saw, cubes (3 x 3 x 2 mm^3) and strips (10 x 2 x 0.24 mm^3) were cut. Smaller grains were produced using a rasp and a sieve tower. The resulting grain sizes were 250–500 µm, 500–1000 µm, and 1000–2000 µm, respectively.

In addition, grain-like samples were prepared from two further regions of the plate, to investigate the homogeneity of the polymer plate. The corresponding regions are marked in Figure 1.

The prepared samples were stored in a constant room climate at a temperature of 20.7 ± 0.2°C and a humidity of 35% ± 2%.

2.2 | Gravimetry by solvent extraction

Solvent extraction of polyamide-6 samples was carried out by Soxhlet treatment with methanol at 85°C for approximately 27 h. Sufficient quantities (within the range of 1.9–2.5 g) of grain-like sample material (grain size 500–2000 µm) taken from the regions one to three of the polyamide-6 plate (see Figure 1) was treated.

Afterwards, the methanol was removed from the dissolved ε-caprolactam by using a rotary evaporator. Subsequently, gravimetric analysis was performed. The ratio of the mass of dissolved ε-caprolactam to the starting sample mass determines the residual monomer concentration.

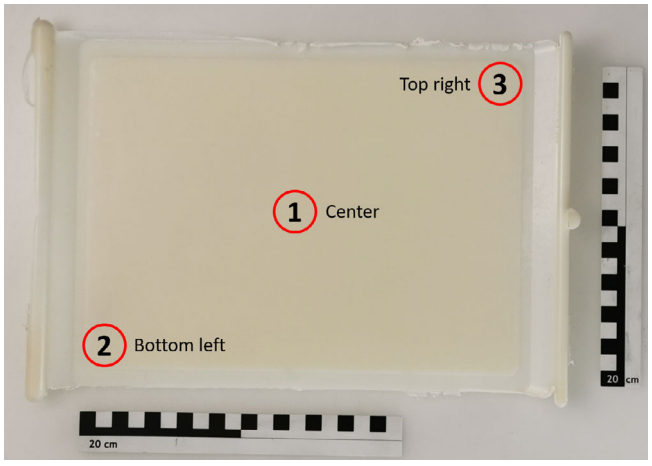

FIGURE 1 In situ polymerized polyamide-6 plate. Regions of sample taking are marked by red circles [Color figure can be viewed at wileyonlinelibrary.com]

2.3 | Thermogravimetric analysis

TGA was performed at a STA 449 F3 Jupiter (Netzsch, Germany). The polyamide-6 samples with initial sample weights of about 30 mg were placed in TG-DTA crucibles made of aluminum oxide (Al_2O_3). For dynamic measurements the samples were heated under helium gas flow (35 or 70 ml/min) to a temperature of 350°C at 5 K/min or to a temperature of 300°C at 2.5 K/min. For isothermal measurements the samples first were dried at 75°C for about 2 h. Then extraction of the residual ε-caprolactam was performed at 160°C for another 3 h. Heating to the target temperatures was performed at a rate of 2.5 K/min. TG signals with a mass resolution of 1 µg were recorded as function of temperature or time. The software Netzsch Proteus version 6.1.0 was used to analyze the TGA-Data.

The STA was coupled with a FTIR ALPHA (Bruker, Germany), which analyzed the type and amount of released gasses as a function of temperature. The spectrometer was mounted directly onto the gas outlet of the STA furnace. In order to prevent condensation of volatile components, all coupling connections were heated to 220°C and the gas cell of the FTIR spectrometer was heated to 200°C. FTIR absorbance spectra were recorded every 11 s with a resolution of 4 cm^{-1} in the wavenumber range from 550 to 4400 cm^{-1}. Data acquisition and evaluation was performed with the software OPUS 7.0 (Bruker, Germany).

A characteristic IR band of ε-caprolactam with minimum overlap to bands of other evolved gas species was identified at 1714 cm^{-1} (see Figure 2). It is generated by a stretch oscillation of carbonyl groups. The absorbance of this band was evaluated by integration relative to the local linear baseline. These absorbance values as function of time, which corresponds to a defined temperature, provide the ε-caprolactam trace.

3 | RESULTS

3.1 | TG/FTIR on polyamide-6

Figure 3 shows an exemplary TG measurement of a grain-like polyamide-6 sample (grain size 250-500 µm) together with the corresponding FTIR trace of gaseous ε-caprolactam. In the low-temperature range between 100 and 200°C a broad maximum (peak maximum at 160°C) is observed in the FTIR ε-caprolactam trace. In the same temperature range the mass decreases and forms a step in the TG signal. Both features result from the escape of residual ε-caprolactam monomer

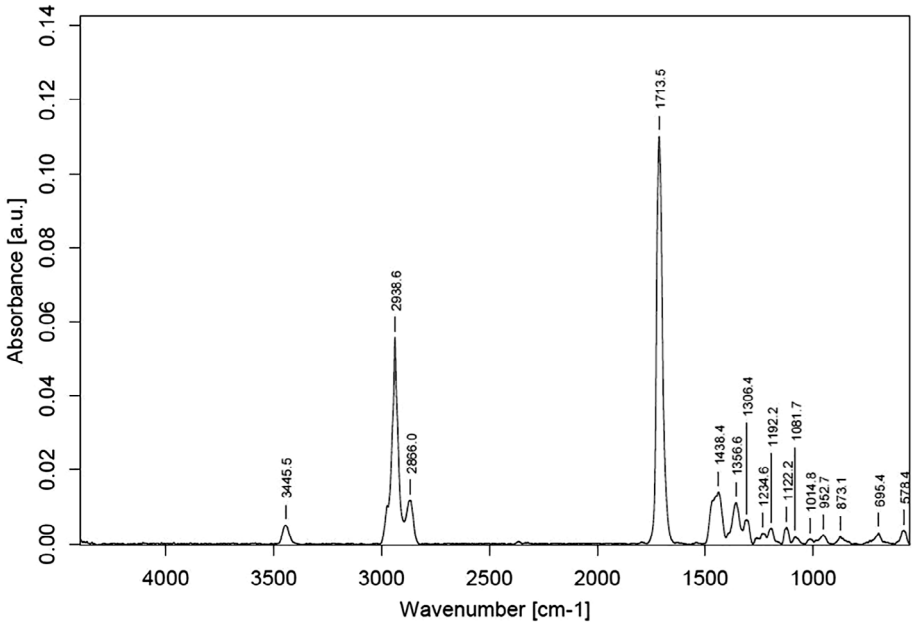

FIGURE 2 FTIR spectrum of ε-caprolactam released during TG measurement of polyamide-6 at a temperature of 250°C. FTIR, Fourier transform infrared spectroscopy; TG, thermogravimetric

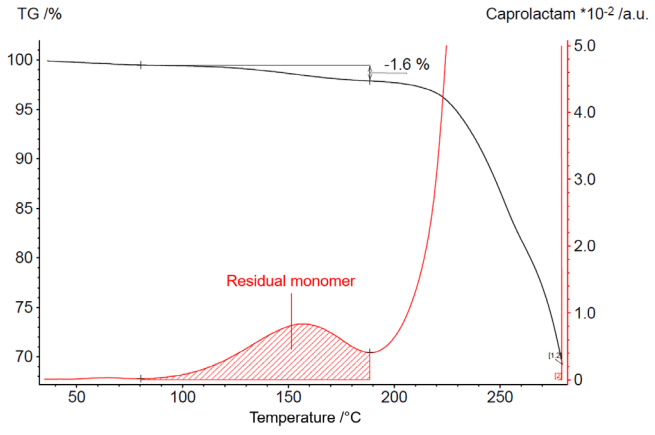

FIGURE 3 TGA coupled with FTIR gas analysis of polyamide-6: Mass loss (TG) and FTIR ε-caprolactam trace (Caprolactam). FTIR, Fourier transform infrared spectroscopy; TGA, thermogravimetric analysis [Color figure can be viewed at wileyonlinelibrary.com]

molecules from the polyamide-6.[32] In addition, FTIR detects low amounts of released water at temperatures below 100°C. This leads to a slight decrease in mass, too, especially at the beginning of the measurement. At temperatures above 200°C the depolymerization of polyamide-6 to ε-caprolactam starts,[32,33] which is reflected in the measurement data by a dramatic increase in the FTIR ε-caprolactam trace and a strong loss of mass. Except for water, in the whole temperature range the FTIR measurement only shows the expected ε-caprolactam bands, no other gasses are detected.

The residual ε-caprolactam monomer concentration of polyamide-6 can be determined by combining the results from TGA and FTIR. The peak in the FTIR ε-caprolactam trace in the low-temperature range (<200°C) defines the range of the residual ε-caprolactam release. The increase of the FTIR ε-caprolactam trace at around 80°C (see Figure 3) marks the beginning of monomer release. The minimum in the FTIR ε-caprolactam trace around 190°C (see Figure 3), indicating the end of the residual monomer release and the start of polyamide-6 depolymerization, is used in the following as upper temperature limit for the quantitative evaluation. The step in the TGA curve in this temperature limits defines the corresponding mass loss, that is, its represents the residual monomer concentration as determined by TGA.

In ref. 21 a different temperature range for the determination of residual ε-caprolactam by TGA is suggested, that is, the range between 100 and 300°C. However, these temperature limits were determined only by TGA measurement. Our investigations demonstrate that FTIR gas analysis is imperative to define the temperature limits for the residual monomer release, in order to avoid overestimating the residual monomer concentration due to ε-caprolactam from the depolymerization of polyamide-6.

To determine the residual caprolactam concentration from the FTIR signal only, a calibration of the FTIR absorbance is performed using combined FTIR/TG on pure ε-caprolactam (as presented in Section 3.2). This allows a quantitative determination of the residual ε-caprolactam concentration by FTIR only. Here, an influence of released water on the measuring result is avoided, since FTIR—in contrast to TGA—only takes into account the signal of ε-caprolactam.

For a quantitative determination of the residual ε-caprolactam monomer concentration in polyamide-6 using TGA coupled with FTIR gas analysis three main aspects have to be addressed: The calibration of the FTIR absorbance of ε-caprolactam, the effect of the measurement

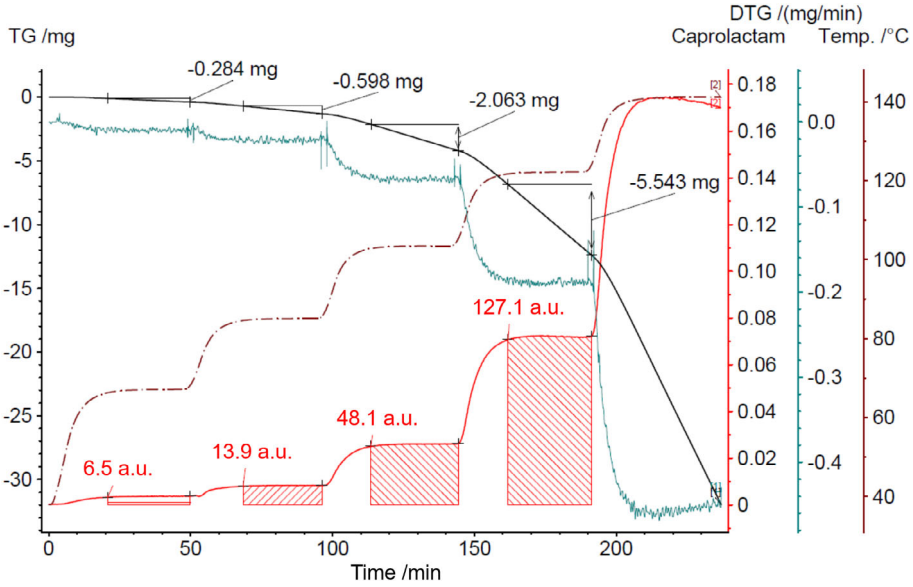

FIGURE 4 Calibration measurement of pure ε-caprolactam at different defined evaporation rates: Mass loss (TG), FTIR caprolactam trace (Caprolactam), mass loss rate (DTG), and temperature (temp). DTG, differential thermogravimetric; FTIR, Fourier transform infrared spectroscopy; TG, thermogravimetric [Color figure can be viewed at wileyonlinelibrary.com]

parameters on the measured data, and finally the influence of the sample geometry on the TGA-FTIR results.

3.2 | Calibration of FTIR absorbance of ε-caprolactam

To quantify the amount of gaseous ε-caprolactam, which is released during thermal analysis, by FTIR analysis a calibration measurement is performed. To this end, a calibration factor between the FTIR absorbance of the characteristic carbonyl band at 1714 cm^{-1} and the corresponding TGA mass loss is determined. The calibration measurement is performed for different concentrations of gaseous ε-caprolactam, since the relation between the FTIR absorption and the concentration does not have to be linear (Beer–Lambert law). Different concentrations were realized by different mass loss rates at different temperatures (see Figure 4). The ε-caprolactam concentrations were chosen to cover the relevant range of gas concentrations occurring during polyamide-6 sample measurements.

130 mg of pure AP-Nylon® Caprolactam flakes with a thickness <1 mm and lateral dimensions varying from 3–5 mm, were placed in an aluminum oxide crucible. Isothermal time intervals at temperatures of 70, 90, 110, 130, and 150°C for 45 min, respectively, were realized (35 ml/min He gas flow). The melting point temperature of ε-caprolactam is 69°C.[35]

The results of the calibration measurements are shown in Figure 4. For each isothermal time interval the mass loss was evaluated at a constant mass loss rate, that is, a constant differential thermogravimetric (DTG) signal. The FTIR ε-caprolactam trace was integrated over the same time interval. Mass loss and time integrated ε-caprolactam absorbance provide the value pairs for the calibration curve.

This calibration curve of pure ε-caprolactam is shown in Figure 5. The calibration curve shows a linear behavior with a correlation square of 0.99996. The slope of the calibration curve of 0.0435 mg/a.u. represents the calibration factor. Based on this calibration the amount of released ε-caprolactam from polyamide-6 can be evaluated by integrating the FTIR absorbance of ε-caprolactam over time and applying the calibration factor.

3.3 | Effects of sample geometry and measurement parameters

The influence of the sample geometry on the TGA and FTIR results at a heating rate of 5 K/min and 70 ml/min He gas flow is shown in Figure 6. The release of gaseous ε-caprolactam is significantly different for cube, strip, and grain geometry (grain size 250–500 μm). This is due to the fact that the residual ε-caprolactam needs short diffusion paths to be able to leave the polyamide-6 sample. If the diffusion paths are too long, that is, due to large samples, a reduction of the released ε-caprolactam is expected.

For the cube sample geometry, the effect of large diffusion paths is most pronounced. Here, in the temperature range below 200°C, which is relevant for the release of residual ε-caprolactam, no mass loss is detected and the FTIR absorbance for ε-caprolactam is zero. According to refs. 32,33,36 depolymerization of polyamide-6 starts at temperatures slightly above 200°C. This is in agreement with our measurement data, where beyond 200°C the mass loss and the FTIR absorbance of ε-caprolactam

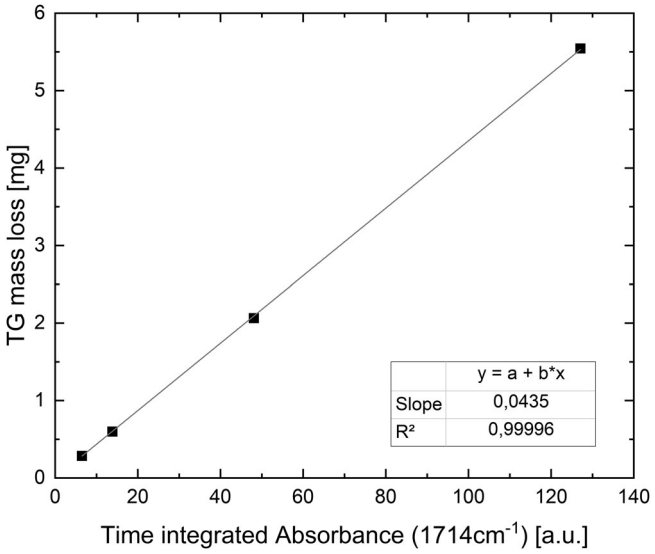

FIGURE 5 TG-FTIR-calibration curve of pure ε-caprolactam. FTIR, Fourier transform infrared spectroscopy; TG, thermogravimetric

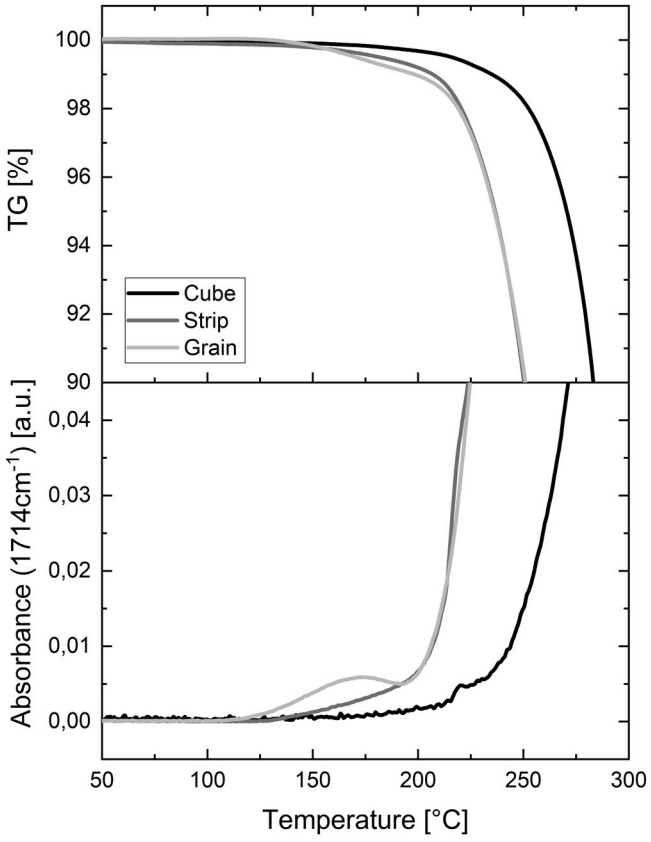

FIGURE 6 TG signal (top) and FTIR absorbance (bottom) of ε-caprolactam for different sample geometries: Cube, strips, and grains. FTIR, Fourier transform infrared spectroscopy; TG, thermogravimetric

increase strongly. Furthermore, our FTIR measurement data show only ε-caprolactam bands, as expected for the polyamide-6 depolymerization to ε-caprolactam.

For the strip geometry, the release of ε-caprolactam starts already at about 125°C, that is, significantly below the depolymerization temperature, indicating the release of residual ε-caprolactam.

For grain-like samples, that is, the smallest sample dimensions with a large surface to volume ratio, a maximum in the residual monomer release can be clearly observed in the FTIR ε-caprolactam trace in the temperature range below 200°C. In the same temperature region the mass decreases and forms a step in the TG signal. Above 200°C the depolymerization of the polymer to ε-caprolactam starts. Consequently, while for the cube and the strip shape samples separation of residual ε-caprolactam and reformed ε-caprolactam is not possible, the measurement on grained polyamide-6 allows clear separation of residual and reformed ε-caprolactam. We assume that a smaller particle size, that is, larger total surface area of the sample, is advantageous for the evaporation of residual ε-caprolactam.

Figure 7 shows the influence of the heating rate and the gas flow on the mass loss and the FTIR absorbance for the same grain-like sample geometry (grain size 250–500 µm). The lower heating rate of 2,5 K/min together with the lower gas flow of 35 ml/min He provide a more pronounced TG step and a more clearly separated residual monomer peak in the ε-caprolactam trace compared to the high heating rate of 5 K/min and the high-gas flow of 70 ml/min. This clear separation is necessary for a reliable quantitative evaluation. This result can be expected, since the low-heating rate allows a more complete diffusion of the monomer out of the sample. In addition, the small gas flow ensures that the concentration of residual ε-caprolactam remains sufficiently high for reliable FTIR absorbance measurement.

In order to further optimize the sample geometry, the release of ε-caprolactam from defined grain sized samples with dimensions of 250–500 µm, 500–1000 µm, and 1000–2000 µm were investigated at a heating rate of 2.5 K/min and 35 ml/min He gas flow. The results are presented in Figure 8. The mass loss is not significantly different for the different grain sizes. In contrast, the maximum in the ε-caprolactam trace becomes more pronounced with decreasing grain size. A further reduction of the grain size to 100 µm with the help of a cryo mill shows no further effect, that is, a saturation of the ε-caprolactam release at grain sizes at 250–500 µm is observed.

In summary, the variation of the sample geometry and the measurement parameters showed that for the method presented here samples with a grain size of 250–500 µm, a heating rate of 2.5 K/min, and a He gas

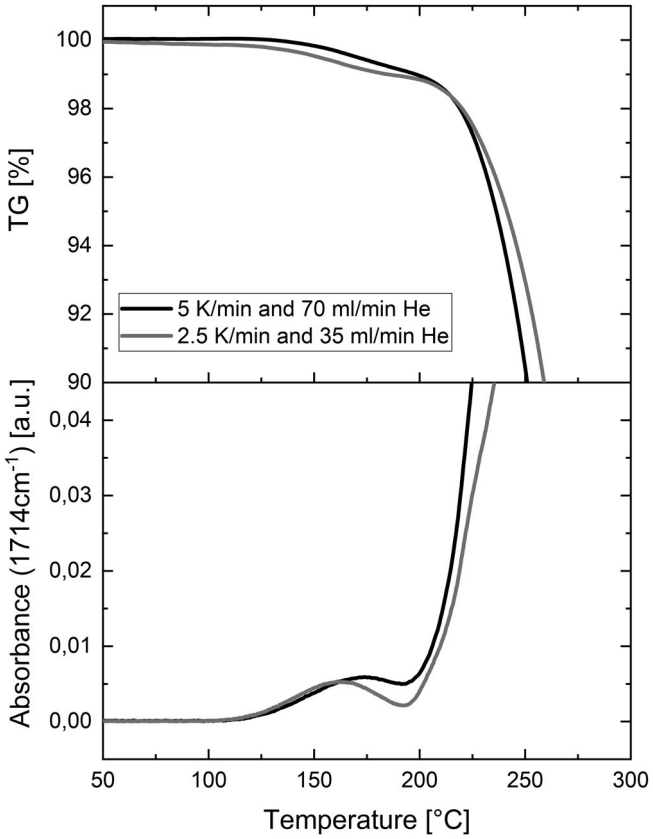

FIGURE 7 TG signal (top) and FTIR absorbance (bottom) of ε-caprolactam for the same grain-like sample geometry and different heating rates and gas flows: 5 K/min with 70 ml/min he gas flow and 2.5 K/min with 35 ml/min. FTIR, Fourier transform infrared spectroscopy; TG, thermogravimetric

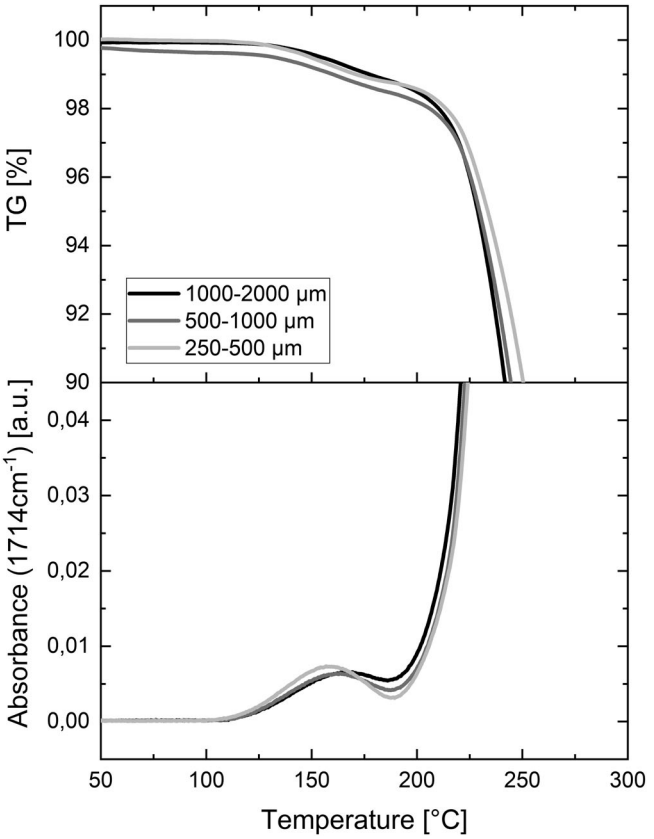

FIGURE 8 TG signal (top) and FTIR absorbance (bottom) of caprolactam at a heating rate of 2.5 K/min and 35 ml/min he gas flow for different grain sizes: 1000–2000 µm, 500–1000 µm, and 250–500 µm. FTIR, Fourier transform infrared spectroscopy; TG, thermogravimetric

flow of 35 ml/min should be used in order to reliably determine the residual monomer concentration of polyamide-6. These parameters were used for all measurements presented in the following.

3.4 | Determination of the residual monomer concentration of a polyamide-6 plate

This new TGA/FTIR method was used to investigate the concentration of residual ε-caprolactam of the in situ polymerized polyamide-6 plate. Samples of three different regions of the polyamide-6 plate (see Figure 1) were examined, to investigate the homogeneity of the plate. The TGA/FTIR results of all three investigated regions are summarized in Table 1. For comparison, also the results from conventional TGA analysis and gravimetry after soxhlet extraction are included in Table 1.

For samples from the center of the polyamide-6 plate (region 1), four TGA/FTIR measurements were performed under identical conditions, in order to determine statistical fluctuations of the TGA/FTIR method. The measurements show an average residual monomer concentration of 1.45 ± 0.02 wt%. Based on the standard deviation, the error of the TGA/FTIR method is estimated to maximal 0.1 wt%.

From the four measurements, the residual ε-caprolactam concentration was also determined by conventional TGA, using the temperature limits determined by FTIR gas analysis. This results in a value of 1.63 ± 0.03 wt%. Here, the error of the TGA method is estimated to maximal 0.1 wt%.

After a TGA/FTIR measurement the sample was cooled down and was measured again. In such a TGA/FTIR control measurement no further monomer ε-caprolactam was released from the polymer in the relevant temperature range below 200°C. This demonstrates that all residual monomer has been removed in the original measurement of the sample.

The TGA/FTIR analysis of the polyamide-6 plate reveals a residual ε-caprolactam monomer concentration of about 1.5 wt% in all investigated regions of the plate, that is, a conversion of 98.5 wt%.

TABLE 1 Residual ε-caprolactam monomer concentration of three different regions of the polyamide-6 plate determined by TGA/FTIR, TGA, and gravimetry after soxhlet extraction

	Residual monomer (wt%) by TGA/FTIR	Residual monomer (wt%) by TGA	Residual monomer (wt%) by soxhlet extraction
1) Center	1.5 ± 0.1	1.6 ± 0.1	2.9 ± 0.3
2) Bottom left	1.5 ± 0.1	1.7 ± 0.1	3.2 ± 0.3
3) Top right	1.5 ± 0.1	1.7 ± 0.1	3.0 ± 0.3

Abbreviations: FTIR, Fourier transform infrared spectroscopy; TGA, thermogravimetric analysis.

In literature, depending on the polymerization temperature and the ratios of activator and initiator, final conversion up to 99 wt% are reported for the anionic polymerization of ε-caprolactam to polyamide-6,[1,22,37–40] which agrees well with our result. The agreement of the residual monomer concentrations at the different positions of the plate demonstrates the high homogeneity of the polymer plate. Both, the low-residual monomer concentration and the high homogeneity underline the high quality of the polyamide-6 plate.

In the following we compare TGA/FTIR analysis with conventional TGA. TGA/FTIR at the central position of the plate results in a residual ε-caprolactam monomer concentration of 1.5 wt%. Evaluation of the TG step results in a slightly higher residual monomer concentration of 1.6 wt%. At all other positions, evaluation of the TG step results in slightly enhanced residual monomer concentrations compared to TGA/FTIR analysis, too. The discrepancy might result from the release of water. The small decrease in mass at the beginning of the TG measurement (see Figure 3) is due to the drying of the sample and the corresponding escape of most of the water, which is also observed in the FTIR measurement in the temperature range below 100°C. Therefore, in the relevant temperature range from about 80°C to about 190°C in addition to the residual monomer ε-caprolactam also small rests of residual water could escape and increase the measured mass loss. Since this effect does not influence the residual monomer concentration determined by FTIR, a higher precision and reliability of the here presented TGA/FTIR analysis is assumed.

It has turned out that external drying of the samples in a vacuum furnace before TGA/FTIR measurement does not improve the accuracy of the measurements, since during drying small amounts of residual monomer ε-caprolactam seem to escape together with the water.

For comparison, isothermal TGA/FTIR measurements were performed, too. First, the sample was dried within the STA setup to eliminate residual water. Drying was performed until the TG mass signal became constant, which took about 2 h. FTIR control guarantees that no monomer ε-caprolactam is released during drying treatment. Then, the sample was treated at a constant temperature of 160°C, that is, at the temperature of the maximum of the ε-caprolactam trace (see Figure 3), to extract the residual monomer. FTIR control guarantees, that only ε-caprolactam is released. Again, heating was performed until the mass became constant, which now took about 3 h. Evaluation of the corresponding TG step results in a residual ε-caprolactam monomer concentration of 1.4 wt%, which is slightly lower than the results determined by dynamic TGA/FTIR and TGA measurements. Possibly low amounts of ε-caprolactam still remain in the sample, since the point of saturation of the TG signal is hard to determine due to the very slow signal change. This aspect and the corresponding high-analysis time of about 8 h represent a disadvantage of the isothermal measurement compared to the dynamic one, which only took about 2 h.

To further verify the presented new method, the TGA/FTIR residual ε-caprolactam monomer concentrations are compared to results from the commonly used gravimetry after soxhlet extraction (results included in Table 1). Three measurements were performed on samples taken from region 1 of the plate. The measurements result in an average residual monomer concentration of 2.89 ± 0.29 wt%. Based on the standard deviation, the error of the soxhlet extraction method is estimated to maximal 0.3 wt%.

For all investigated regions of the plate, the residual monomer concentrations as determined by gravimetry are higher than that from TGA/FTIR. This might be due to the fact that the solvent methanol not only removes the residual monomer ε-caprolactam, but also dissolves smaller oligomers[9,10,23,41] and stored water. This results in an additional contribution to the mass of the dissolved material, which falsifies the results.

In contrast, since TGA/FTIR provides the exact knowledge of the analyzed gas species it results in a significantly higher reliability and precision. The influence of other types of molecules, that is, water or small oligomers, can be excluded.

In addition, it should be noted that the common method of gravimetry after solvent extraction is very time consuming. In particular, solvent extraction by Soxhlet treatment can take more than 24 h. In comparison, the here presented new TGA/FTIR method, which only takes about 2 h, is much faster and thus suitable for routine polymer analysis.

4 | CONCLUSION

TGA in combination with FTIR gas analysis was used to analyze the residual monomer concentration of ε-caprolactam in polyamide-6. This combination of FTIR and TGA allows a quantitative, reliable, fast, and fail-safe determination of the mass of residual ε-caprolactam. Sufficiently small heating rates (here 2.5 K/min, helium gas flow of 35 ml/min) and powdery samples (here grain size 250–500 µm) guarantee high-precision measurements. In the presented investigation the method allowed us to demonstrate the low-residual monomer concentration of 1.5 wt% and the high homogeneity of the polyamide-6 plate.

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