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Rapid microwave induced depolymerization of polyamide-6

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Abstract

Polyamide-6 (PA-6) depolymerization was performed using microwaves as the energy source for the acid catalysed hydrolysis, with phosphoric acid as the catalyst. Microwave irradiation of 200 W was applied for 12–23 min to a reaction mixture in a sealed reaction vessel. After 15 min of irradiation PA-6 was completely solubilized. The product mixture consisted of more than 90% ϵ-aminocaproic acid (ACA) and its linear oligomers, with a minor part consisting of cyclic products. The product mixture was analysed by chromatographic and spectroscopic methods. With longer irradiation time or more acid, there was a shift toward higher concentrations of ACA and its dimer, as well as a decrease in the concentrations of higher oligomers. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Polyamide-6; Microwave; Depolymerization

1. Introduction

Polyamide-6 is a widely used engineering polymer. Due to the relatively high price of its monomer, ϵ-caprolactam (CL), as well as the polymer itself, it is economically desirable to recycle it through chemical or mechanical methods. Recently two chemical industry alliances, including major PA-6 manufacturers, announced plans for setting up large scale recycling plants for PA-6 from waste carpets [1,2]. One of these is based on a proprietary process for depolymerization of PA-6 to CL, which will then re-enter the polymerization process. The monomer CL is the cyclic form of ϵ-aminocaproic acid.

PA-6 depolymerization methods are based on a reaction in which a reagent with reactive polar groups opens the amide linkage in the polymer backbone [3,4]. Water is the most common reagent. It was recently used by Bassler and Kopietz [5] as superheated steam at 305°C and 12 MPa to convert the polymer to CL with a 96% yield in 55–60 min. Reagents such as glycols [6] and amines [7] have also been used. The reactions are catalysed by strong acids or bases, of which phosphoric acid is the most commonly used [8]. In general, depolymerization takes place at high temperatures and pressures and requires long reaction times—all factors that increase the technical difficulty, as well as the cost of the process [9].

Microwaves have been successfully applied to a number of classical reactions and have shortened reaction times, as well as changed product compositions [10]. Microwaves were recently shown by our group to be effective in poly(ethylene terephthalate) solvolysis, with complete depolymerization achieved in 5–10 min [11,12]. Microwaves were also reported as the energy source for a semi-industrial scale thermolysis plant for poly(methyl methacrylate) waste with monomer retrieval [13]. In general, with a proper choice of substrates, microwaves can provide rapid heating throughout the entire volume of a reaction mixture, coupled with specific kinetic effects.

In this paper we present preliminary results describing a novel rapid method of PA-6 depolymerization based on microwave energy use. Microwaves were applied to a conventional PA-6 depolymerization system employing concentrated phosphoric acid. Besides its catalytic activity phosphoric acid has a very high dipole moment, which makes it an excellent microwave absorbent. Depolymerization products were fully characterized.

2. Experimental part

Depolymerization experiments were carried out in a Milestone MEGA 1200 laboratory microwave oven equipped with temperature and pressure sensors that can be inserted directly into the sealed 100 ml PTFE reaction vessels. Samples were irradiated for 12–23 min with 200 W pulsed microwave irradiation power. Depolymerization products were characterized by IR spectroscopy and

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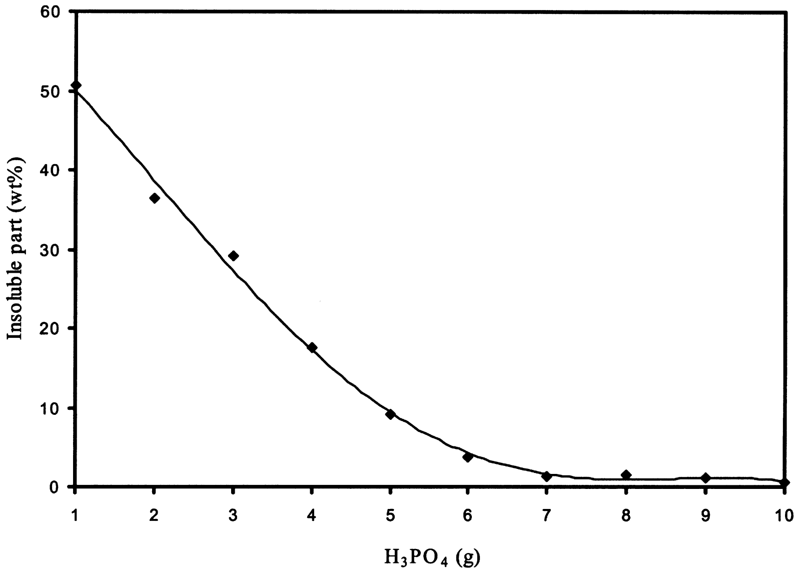

Fig. 1. Dependence of the amount of insoluble depolymerization products vs. acid addition at 20 min 200 W microwave irradiation.

HPLC (Hewlett-Packard Series 1100) using UV detection at 200 nm. HPLC analyses were performed at 25°C on a C-18 column (Nucleosil, Macherey–Nagel). The mobile phase (flow rate 1 ml/min) was gradually changed from 15 to 50% aq. acetonitrile over 14 min [14]. Additional analyses were done by gas chromatography (Perkin Elmer 8700) and linear species were detected by LC–MS (Finnigan LCQ) with electron spray ionization. The method will be fully described in a future paper.

Reaction mixtures consisted of 10 g PA-6, 10 g water and 1–10 g of conc. H_3PO_4. Commercial PA-6 (Julon-Aquafil: $\bar{M}_n = 13,000$ g/mol and $\bar{M}_w = 59,000$ g/mol) was ground to 0.5–1 mm particle size and used without further preparation. All chemicals used were of analytical grade and distilled water was used. It should be noted that phosphoric acid is a very good absorbent of microwave power and should be used with caution and consideration to prevent equipment failure or other accidents.

After irradiation, the samples were cooled to room temperature, neutralized with 3 M KOH(aq.) and diluted with water to 200 g total weight. The mixture was heated to boiling and filtered. The solution was cooled to 25°C overnight, after which any precipitate formed was filtered off. Both filtrates containing the remaining polymer and high oligomers were dried to a constant weight at 60°C and weighed. ϵ-CL and its lower oligomers (up to the hexamer) are soluble in water [15,16] and were retained in the aqueous solution. Phosphates resulting from neutralization were removed by methanol extraction (2 × 100 ml, reflux). The solution was then dried to yield low molecular

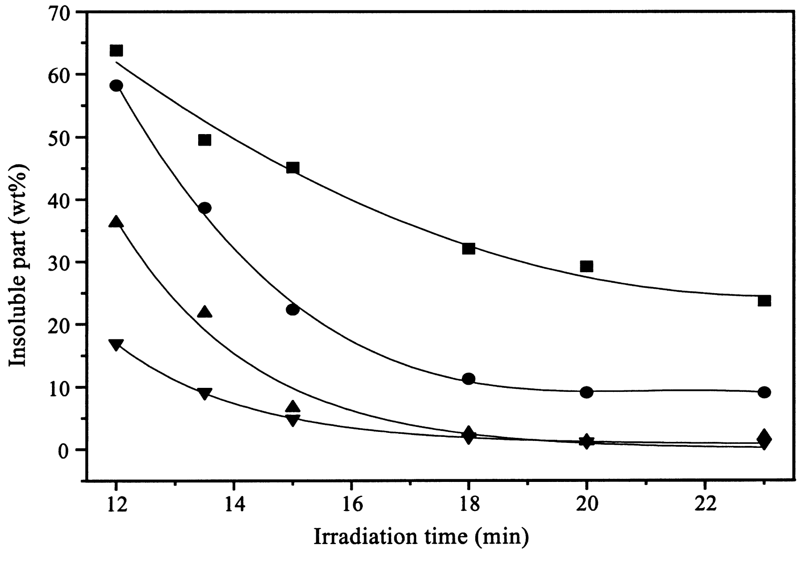

Fig. 2. Effect of irradiation time variation on depolymerization product composition at constant acid content of 3 (■), 5 (●), 7 (▲)and 9 g (▼) of acid.

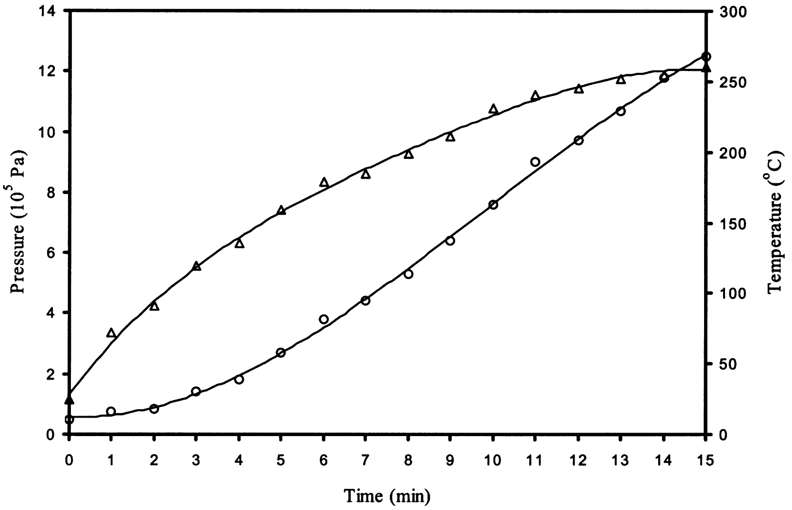

Fig. 3. In situ pressure (○) and temperature (Δ) during 15 min 200 W depolymerization in mixture with 7 g of acid.

weight cyclic and linear depolymerization products that were used in the analyses.

3. Results and discussion

A series of measurements was performed at a constant irradiation time of 20 min, while the amount of added acid was varied from 1 to 10 g. Fig. 1 shows the amount of insoluble depolymerization products as the percent of starting PA-6 vs. acid addition. The solubilization efficiency increased linearly up to 6 g of added acid and is close to complete with 7 g of acid. Further increases in acid addition do not influence the solubilization significantly. Fig. 2 shows the effect of irradiation time variation on reaction mixtures with a constant acid content. Acid additions of 3, 5, 7 and 9 g were used. Results indicate a rapid depolymerization between the twelfth and fifteenth minutes of irradiation. Longer irradiation times improved the yield of water soluble products at a substantially lower rate. These results indicate that depolymerization is most effective with 7 g of acid and an irradiation time of 15 min. These results are in agreement with previous reports of polyamide hydrolysis showing a strong influence of temperature and solution acidity on monomer yields [17].

The reaction conditions were characterized by in situ measurement of temperature and pressure during irradiation. The results of measurements performed in mixtures with 7 g of acid are shown in Fig. 3. During 15 min of irradiation the temperature increased logarithmically to a maximum value of 260°C while the pressure dependence showed exponential growth that reached 1.27 MPa at the end of irradiation. The increase of pressure is most likely linked to the appearance of low molecular weight species as the depolymerization proceeds. In a mixture with 9 g of acid the maximum temperature and pressure after 15 min were 302°C and 2.25 MPa, respectively. Heating above 300°C was generally avoided for safety reasons, due to use of PTFE reactors. The pressures achieved in our experiments are well below those suggested for effective non-catalysed hydrolysis (10–12 MPa) [5] but could be raised in future experiments to the 7 MPa the reactors are rated to withstand. Replacing phosphoric acid with hydrochloric acid (9 g HCl,

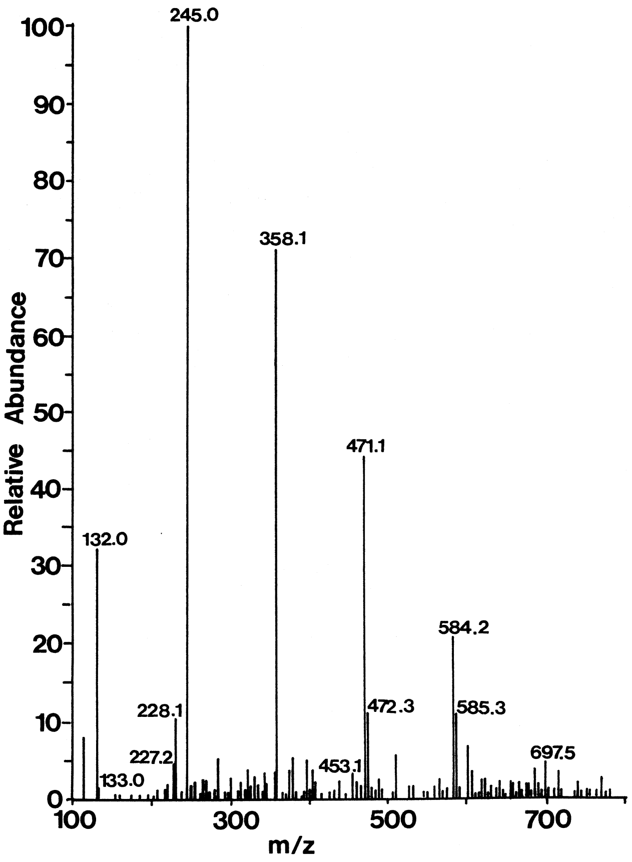

Fig. 4. LC–MS spectrum of depolymerization products (20 min, 200 W, 9 g acid).

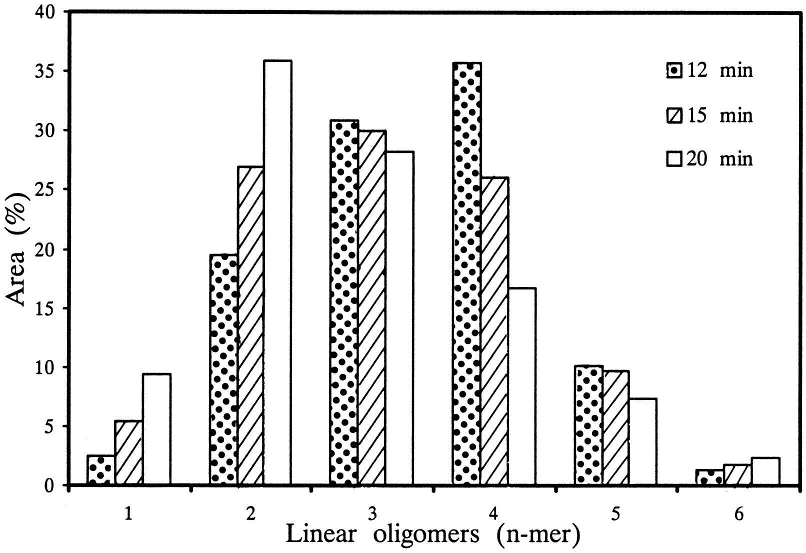

Fig. 5. Relative content of linear oligomers in depolymerization products obtained with irradiation times of 12, 15 and 20 min and 9 g acid addition.

15 min at 200 W) gave a maximum temperature of 216°C and pressure of 0.71 MPa. These results confirm the importance of phosphoric acid as an excellent microwave absorbent.

HPLC and GC analyses on the water soluble products gave evidence of CL and the cyclic dimer. In the series with 20 min irradiation, the CL and cyclic dimer concentration were highest in samples with 1 g acid: 1.6 and 0.15%, respectively. With 9 g acid the concentration of both species decreased to 0.5% for CL and $<0.1\%$ for the cyclic dimer. Analysis of the commercial grade starting material, however, showed a presence of 0.3% CL and 0.2% cyclic dimer. These results indicate that mild conditions (i.e. lower acid addition) cause the formation of a limited amount of cyclic species but harsher conditions result in their disappearance—most probably they are converted into linear species. The simultaneous disappearance of cyclic compounds, as well as the polymer, is in agreement with the reported differences in amide bonds that are either part of a cycle or linear chain. The amide in CL was shown to be 10 times as reactive as the chain amide bond [18].

More importantly, the low total amount of cyclic species indicated that linear species, which could not be detected by the used analytical systems, were the main depolymerization products. Their presence was confirmed by means of a simple chemical test (Hinsberg test) [19] and IR spectroscopy showing characteristic peaks of the linear end-groups (1540 and 2210 cm^{-1} for $-\mathrm{COO}^-$ and $-\mathrm{NH}_3^+$, respectively). Direct evidence of linear products and their distribution was obtained by LC–MS. Fig. 4 shows the mass spectrum of depolymerization products from a reaction mixture with 9 g acid irradiated for 20 min. Peaks at m/z 132, 245, 358, 471, 584 and 697 correspond to linear species up to a hexamer while peaks at 114 and 227 correspond to CL and the cyclic dimer. Lengthening the irradiation time or increasing acid addition shifted the composition toward ACA and low oligomers. Fig. 5 shows the shift caused by irradiation time increase in reaction mixtures with 9 g of acid.

4. Conclusions

To our knowledge, this is the first report of an application of microwaves as the energy source for achieving PA-6 depolymerization. The presented results show this application to be effective under classical conditions with phosphoric acid as the catalyst. The polymer was depolymerized in the relatively short time of 20 min and gave rise to mainly linear products ranging from ACA to its hexamer. The combined analytical procedures including HPLC, GC and LC–MS allowed the identification of both cyclic and linear products.

The subject of a future study will be the extension of the method to a different set of conditions of programmed irradiation and selection of catalysts and reagent mixtures which will use microwaves to their full potential. An additional improvement over the efficiency of the described system is expected by the introduction of continuous monomer extraction, which will shift the equlibria toward low molecular weight products.

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