

LC-MS analysis of oligomers as potential migrants in polycondensate-type food contact polymers

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Introduction

Oligomers are side products of the polymer synthesis or formed through post-production degradation processes^[1]. Present in plastics food contact materials the low molecular weight fraction of oligomers (< 1000 Da) can potentially migrate into the packed food or beverages. Oligomers are not explicitly listed in EU Regulation 10/2011^[2] but must be analysed and quantified to enable evaluation whether their migration potential is in compliance with the general article 3 of the EU Framework Regulation 1935/2004^[3]. Therefore analytical methods for identification and quantification of oligomers are needed. Challenging is hereby the growing number of possible oligomers due to the increasing number of (co)monomers (figure 1 shows some examples) which are authorized for the use in the production of food contact polymers.

Experimental Procedure

Oligomers obtained by solvent extracts from two different polycondensates were subjected to hydrolysis for various time periods (1h, 2h, 3h, 4h, 5h, 2d) and various NaOH concentrations (0.2 M, 0.4 M, 0.6 M, 0.8 M). Neutralization of the samples was achieved with Dowex (50WX2, 50-100mesh). For comparison purposes oligomers were stored in water at room temperature.

Analyses were conducted using an Acquity UPLC system coupled to a Synapt G2Si (Waters).

• Oligomers

Column: Acquity UPLC HSS T3 1.8 μ m 2.1x100mm (waters); LC conditions: 0.5 ml/min, solvent A: methanol, solvent B: water, from 50% A to 100% A in 2.5 minutes, keep at 100% for 1 min and then to 50% in 0.1 min and keep at 50% for 1 min; ionization: ESI positive; Mass range: 50 – 1200 m/z.

• Acids

Column: Luna 5u Hilic 200A 3x150 mm (Phenomenex); LC conditions: 0.6 ml/min, solvent A: ACN+5mmol NH₄CHOO, solvent B: water+5mmol NH₄CHOO, start 100% A, isocratic for 2 min, to 55% A in 5 minutes, keep at 55% for 2 min and then to 100% in 0.1 min and keep at 100% for 2 min; ionization: ESI negative; Mass range: 50 – 200 m/z.

Results and Discussion

Due to different responses of different substances in LC-MS and the extensive amount of different oligomers potentially present in one polycondensate a method is suggested combining two intentions: firstly, identification of the oligomers and characterisation of their molecular weight distribution pattern with LC-MS. Secondly, hydrolysis of the oligomers and determination of the common hydrolysis product which is a monomeric unit for example the acid component. Six different oligomers were detected in the extract of polycondensate I and nine in the extract of polycondensate II. The substances were confirmed by accurate mass (< 5 ppm) and MS/MS experiments. The oligomer distribution pattern was evaluated with LC-MS and is shown in figure 2 and 3. No acid was formed during the storage time in water at room temperature suggesting that hydrolysis did not take place under this condition.

For polycondensate I oligomers different NaOH concentrations for one hour were tested. Additionally the hydrolysis was studied in dependence of the time at the same NaOH concentration. Most oligomers were hydrolysed after one hour at 0.6 M NaOH and five hours at 0.2 M NaOH. Similar trends were observed for polycondensate II oligomers.

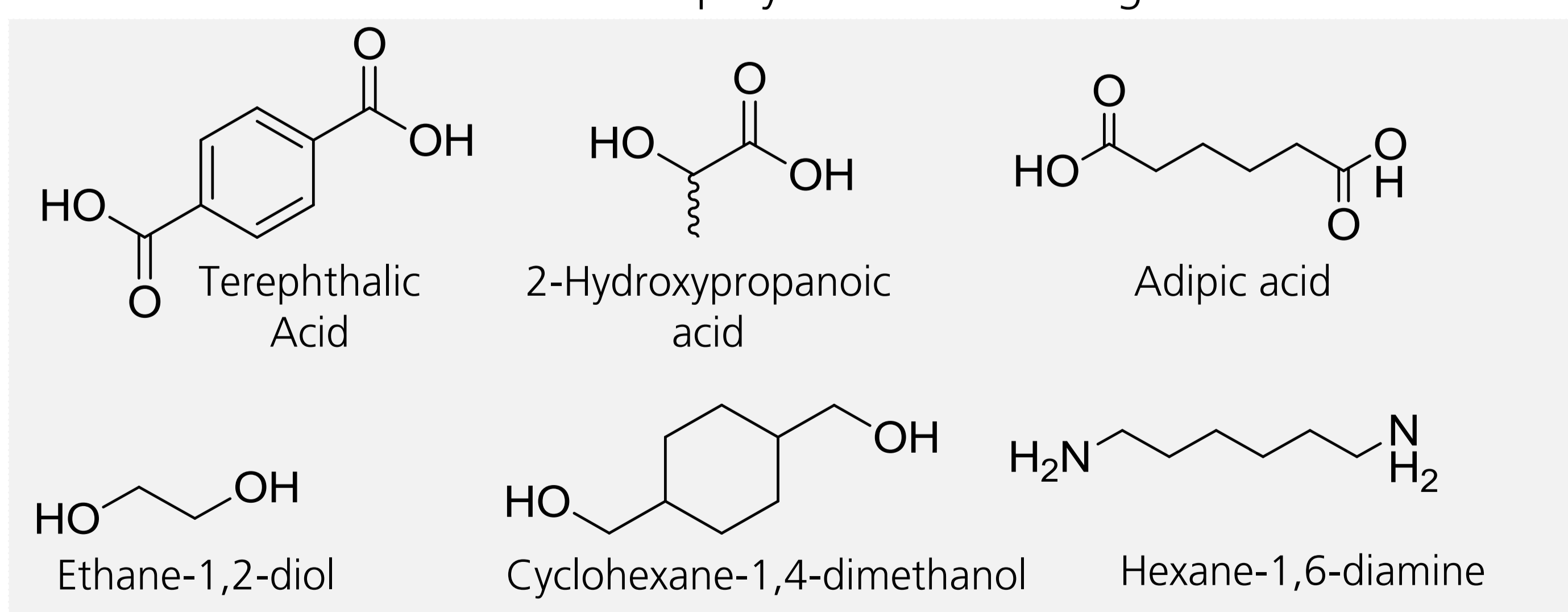


Figure 1: Examples of acids, diols and a diamine used as monomers for food contact polycondensates.

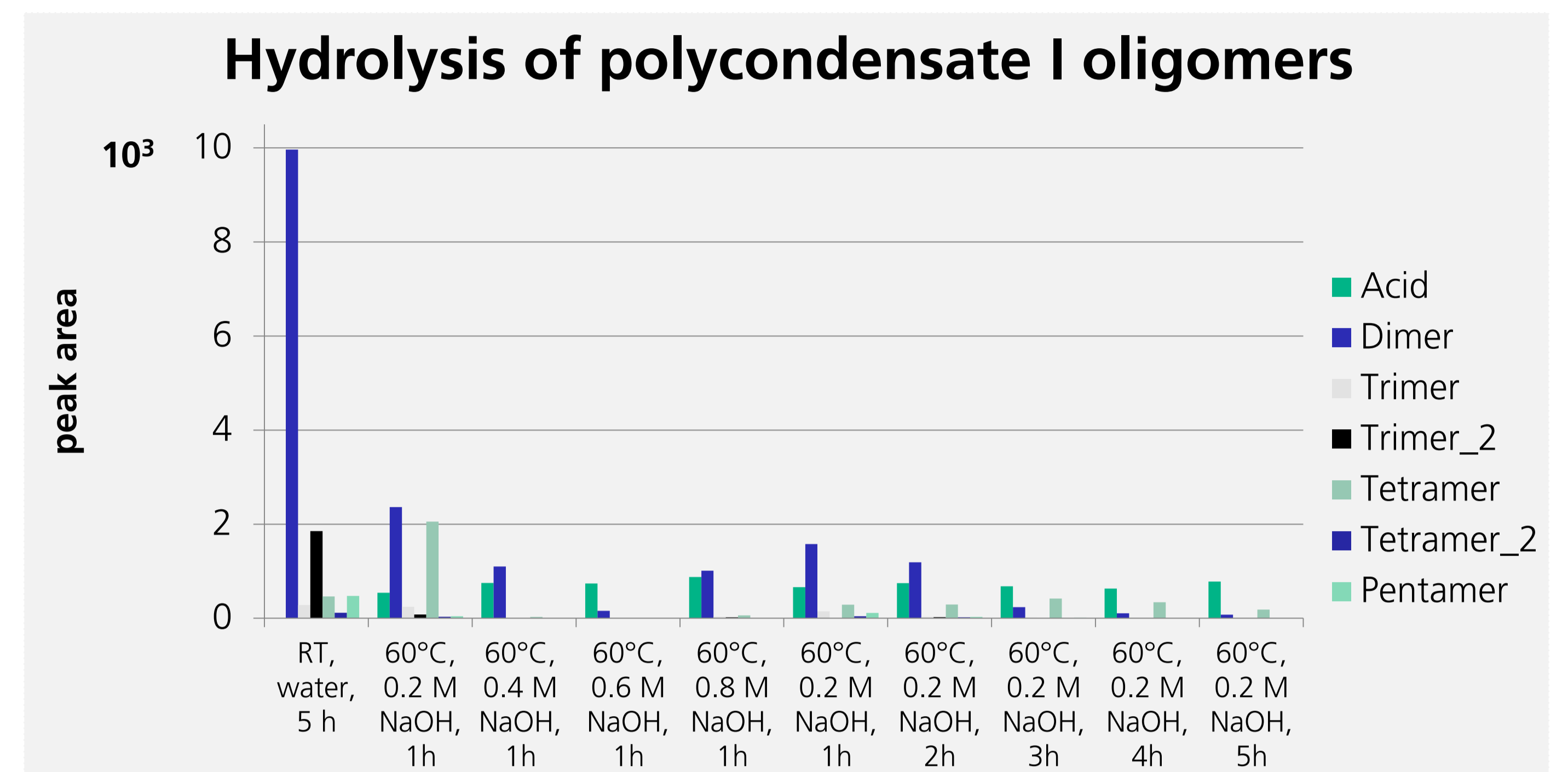


Figure 2: Hydrolysis of polycondensate I oligomers at 60°C and various NaOH concentrations and time periods (n=1).

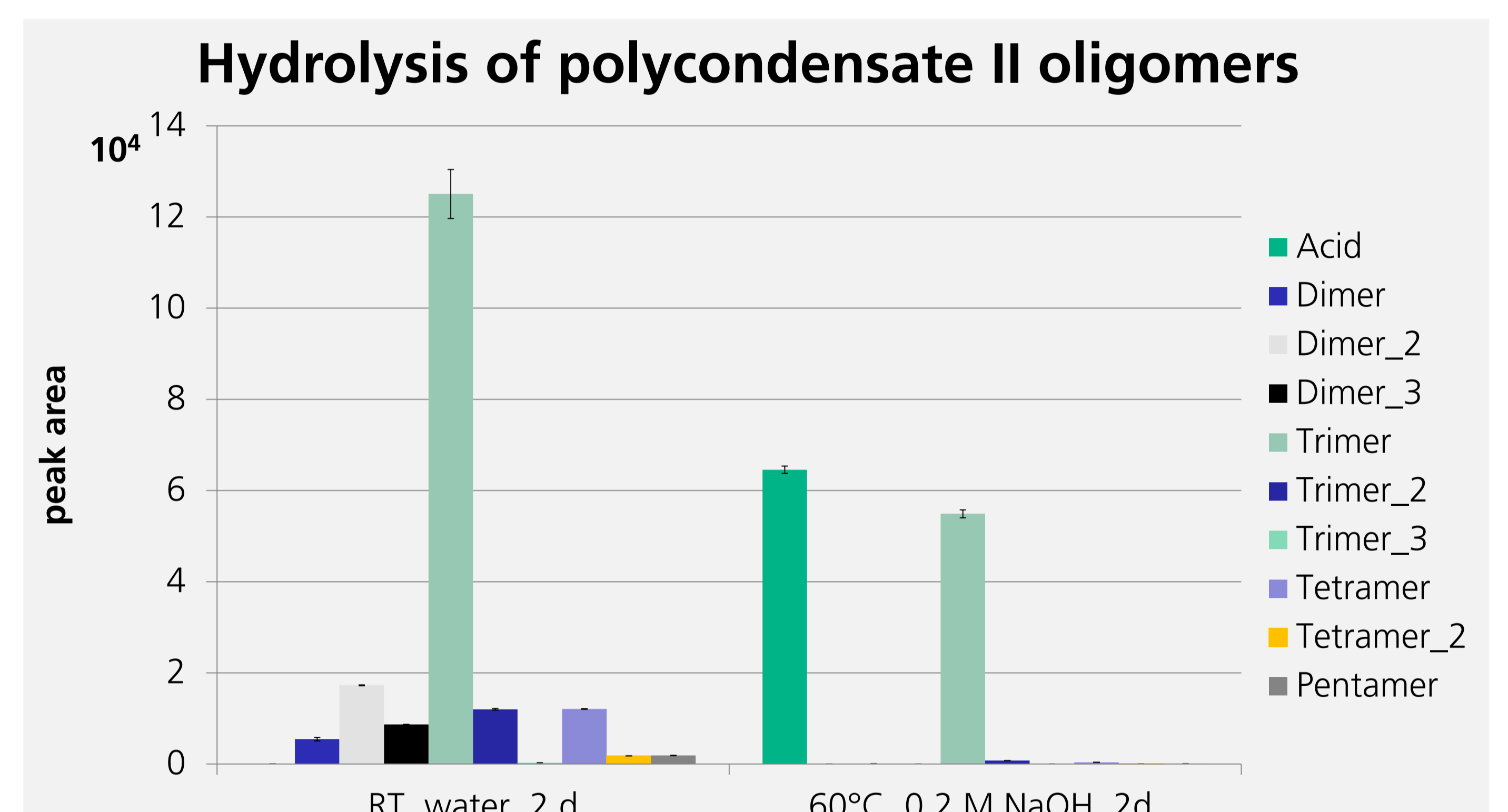


Figure 3: Hydrolysis of polycondensate II oligomers at room temperature in water and at 60°C in 0.2 M NaOH for 2 d (n=2).

Results and Discussion (continuation)

Longer time periods were tested for the polycondensate II extract to ensure complete hydrolysis since some oligomers were still present after hydrolysis for five hours. It could be shown that after two days no oligomers could be detected in the samples, except the trimer for which the method still has to be optimized.

Conclusions

The results of this study show that oligomers present in polycondensates can be individually identified with LC-MS. Total quantification is possible determining the monomer content (acid) after complete hydrolysis which was best obtained using a NaOH concentration of 0.2 M at 60°C for two days.

References

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- [2] EU (2011). Commission regulation (EU) No 10/2011 of 14 January 2011 on plastic materials and articles intended to come into contact with food.
- [3] EU (2004). Regulation (EC) No 1935/2004 of the European Parliament and of the Council of 27 October 2004 on materials and articles intended to come into contact with food and repealing Directives 80/590/EEC and 89/109/EEC.

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