Reactivity Study of Multi-Functional Monomers for the Development of Water-Dispersible Polyesters

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Introduction

Although polyesters have been investigated for more than a century, their versatility and wide applicability still attract scientists. Nowadays, research focuses on bio-based monomers, bio-degradable products and more environmentally friendly polycondensation processes. In order to systematically investigate new functional building blocks, a deep understanding of monomer reactivities is necessary which can be achieved by the combination of NMR methods and MALDI mass spectrometry [1].

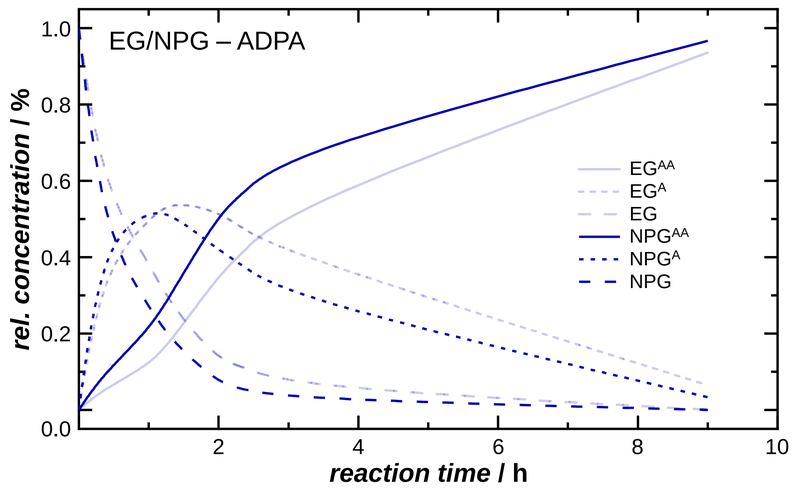


Figure 1 (above): For most diols like ethylene glycol (EG) and neopentyl glycol (NPG) specific peaks in ^{1}H NMR are observed for monomer, monoester (^{A}) and diester (^{AA}). Results indicate higher reactivity of NPG which is further used for reaction with tartaric acid.

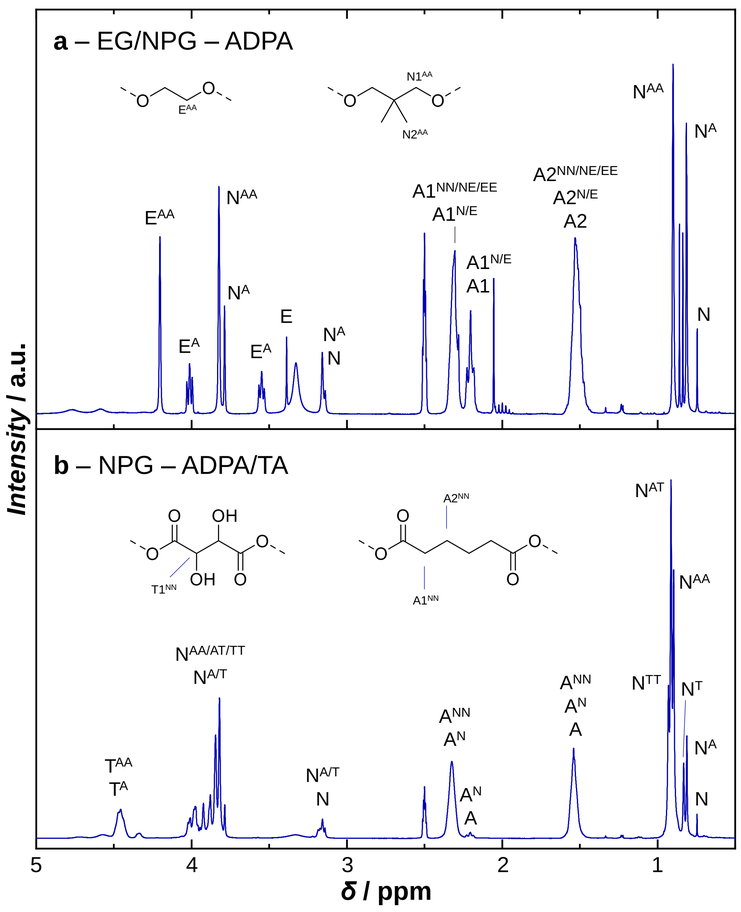
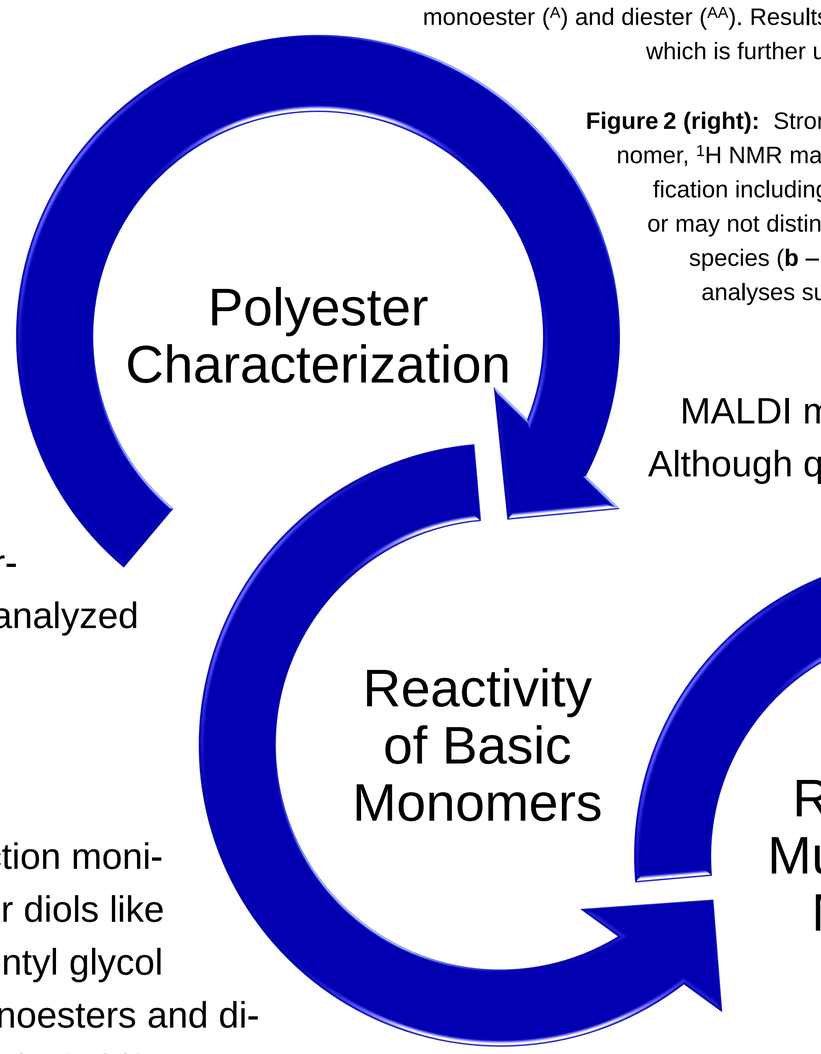


Figure 2 (right): Strongly depending on the kind of monomer, ^{1}H NMR may reveal different extend of esterification including reaction partners (**a** – EG, NPG) or may not distinct between monomer or esterified species (**b** – ADPA) which demands additional analyses such as MALDI mass spectrometry.

Experimental

Polyester are synthesized via mass polycondensation. A standardized procedure with reaction temperatures of 140–200 °C and frequent sampling is applied. Next to conventional methods such as end group titration and size exclusion chromatography, intermediate and final products are analyzed using ^{1}H NMR and MALDI MS.



Results

As Figures 1 and 2a show, reaction monitoring via ^{1}H NMR works well for diols like ethylene glycol (EG) and neopentyl glycol (NPG) because monomers, monoesters and diesters significantly differ in chemical shifts. However, this phenomenon is less observed for carboxylic acids (Fig. 2b). Proton shifts of adipic acid (ADPA), for example, are only affected if directly neighboring a COOH or COOR group. This requires additional analytical methods like MALDI.

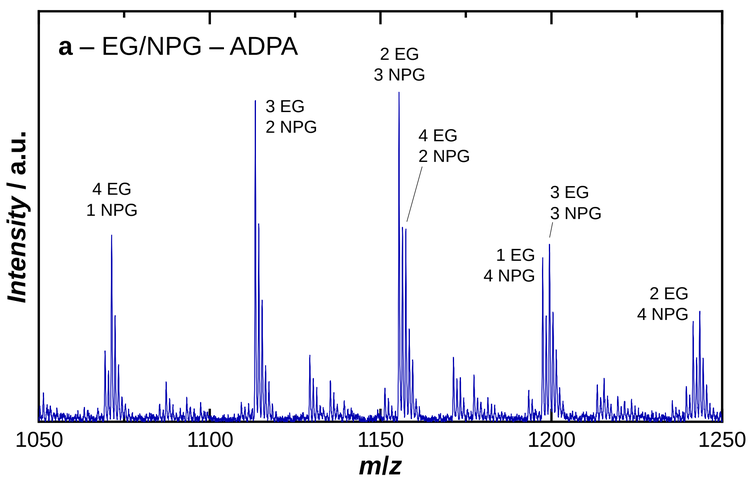
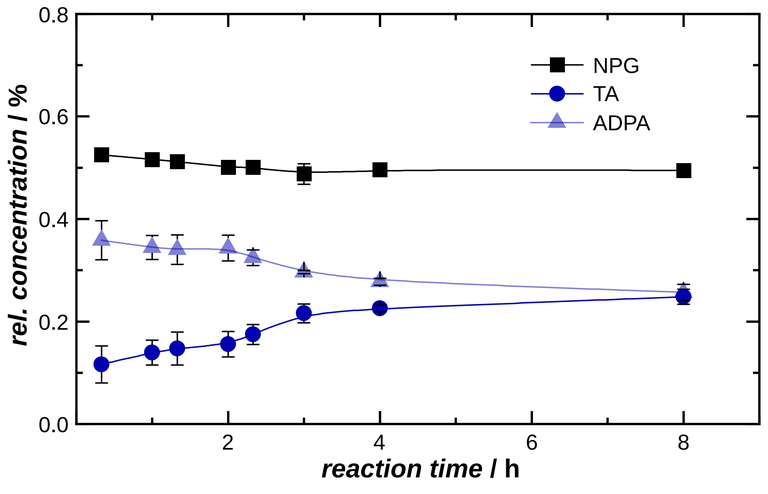


Figure 3 (left): MALDI mass spectra of polyesters with **a**) ethylene (EG) and neopentyl glycol (NPG) and **b**) adipic (ADPA) and tartaric acid (TA). Peak integration allows for estimation of polyester compositions.

Figure 4 (below): Composition of neopentyl glycol, adipic acid and tartaric acid polyester determined via MALDI mass spectrometry. Due to peak overlapping in ^{1}H NMR, MALDI is the method of choice.



MALDI mass spectra of investigated polyester systems are shown in Figure 3. Although quantitative applications of MALDI are rare, suitability has been shown for unsaturated polyesters [1] and is continuously tested on new systems using a software which is significantly decreasing the time needed for spectrum interpretation [2]. Polyesters like EG/NPG-ADPA may be used for validation of MALDI analysis. In this example 51.0% EG content (MALDI) is perfectly consistent with the NMR result (50.5%).

The concept is further applied to biobased multifunctional monomers such as tartaric acid. In reaction with adipic acid, NMR only allows for reaction monitoring via splitting of NPG methyl protons which is prone to inaccuracies. Hence, reaction monitoring using MALDI is superior. Figure 4 shows the preferred incorporation of adipic acid over tartaric acid. With this information, reaction conditions can be systematically altered to achieve desired polyester composition.

Conclusion

To systematically develop new polymers such as bio-based, water-dispersible polyesters, a thorough understanding of the reactivity of basic and multifunctional monomers is required. Only the combination of MALDI mass spectrometry and ^{1}H NMR provides the essential information on polyester compositions. Knowing the effects of reaction parameters on incorporation of green functional building blocks allows targeted optimization of structure and material properties.

References
[1] Saller K. M., Gnatiuk I., Holzinger D., Schwarzinger C., Semiquantitative Approach for Polyester Characterization Using Matrix-Assisted Laser Desorption Ionization/Time-of-Flight Mass Spectrometry Approved by ^{1}H NMR, *Anal. Chem.* (**2020**), 92, 15221–15228.
[2] Saller K. M., Pernusch D., Schwarzinger C., Novel software for simplified interpretation of MALDI mass spectra of complex polymer systems, to be submitted in May 2022.