Reaction Control of Polycondensations via Monomer Quantification by HPLC-MS and ^{1}H-NMR Spectroscopy

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Conclusion

^{1}H-NMR is a useful analytical method for screening the reaction progress of polycondensation reactions. For diols, not only the monomer concentrations but, further, information about the number of terminating groups can be determined. As peaks for acid components are not clearly distinguishable, an alternative method needs to be tested for monomer quantification. Additionally, with increasing complexity of the polyester and the reaction progress, evaluation gets more and more problematic.

HPLC-MS provides less information about the polyester structure, but the monomer concentrations can be determined even if a high number of different monomers is used, and polyester systems get more complicated. Therefore, a combination of these two methods seems ideal to master the challenges of this complex reaction monitoring task.

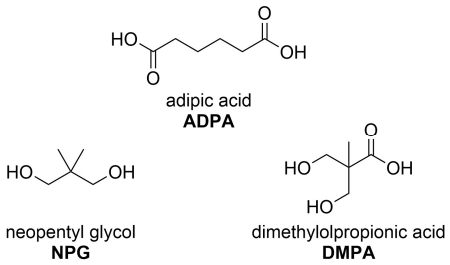

Fig.1: Structures of used monomers for the polyester synthesis.

Introduction

A complete conversion of monomers is a strongly desired factor in polymer reaction engineering. Residual monomers can affect physical properties like accelerated degradation, changes in glass transition temperature or loss of optical or mechanical properties. Furthermore, a full conversion of monomers to polymer is an important factor because in some cases potentially hazardous residuals have to be removed in a separate step. Different polyesters were synthesized to investigate the incorporation of free carboxylic acids into linear polymer chains. To monitor the reaction progress, various spectroscopic or chromatographic methods can be used, which mainly depend on the used monomers.

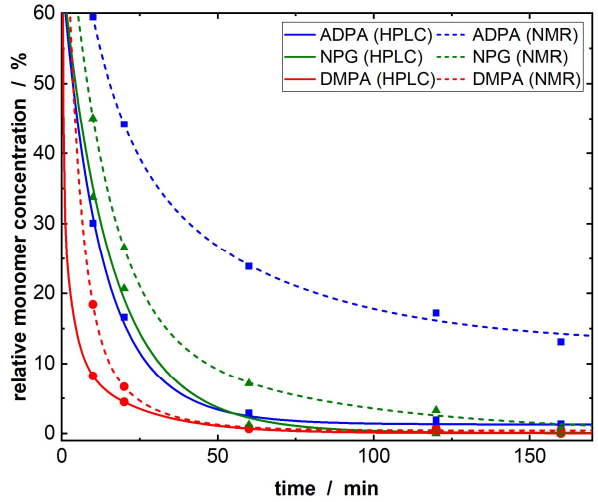

Fig.2: Decrease of monomer concentration over a reaction time of 170 min in a three-component polyester determined by HPLC-MS and ^{1}H-NMR spectroscopy. The results for the diol components are quite comparable. The free adipic acid concentration is overestimated, due to an overlap of the methylene peaks of free monomer and terminating groups.

Experimental

Two analytical methods for quantification of monomers were compared: high performance liquid chromatography (**HPLC**) and proton nuclear magnetic resonance spectroscopy (**^{1}H-NMR**). Therefore, samples were taken over the whole reaction time during the synthesis of different polyesters and characterized separately.

Polyesters were synthesized via melt polycondensation of two to four monomers. Amongst them were adipic acid (**ADPA**) as diacid, neopentyl glycol (**NPG**) as diol and dimethylolpropionic acid (**DMPA**) as bifunctional compound (Fig. 1).

^{1}H-NMR spectroscopy was performed in DMSO-d_6 on a Bruker 300 MHz system. HPLC was performed on a Thermo Surveyor HPLC with a reversed phase C18 column in an acetonitrile/water gradient and coupled to a Thermo Scientific LTQ Orbitrap Velos mass spectrometer.

Results and Discussion

The reaction progress can be visualized by plotting the relative change of the monomer concentration, whereas 100% is the initial amount for each individual monomer. In Fig. 2 the progress of a three-component polyester over a reaction time of 170 minutes is shown. For the diol components, HPLC (solid line) and ^{1}H-NMR results (dashed line) are quite comparable. The free monomers are clearly visible as single peaks in the NMR spectra (Fig. 3) and monomer, monoester (terminating groups) and diester ratios can be monitored (Fig. 4).

Since adipic acid monomer and monoester exhibit the same proton shift, the monomer content is overestimated from the NMR method. The same problem can be observed for the other acid components. With HPLC-MS only the free monomers are considered. Especially for quantification of the acids and for more complicated polyester systems with a higher number of monomers, HPLC-MS is a superior method and overall, a good addition to NMR spectroscopy.

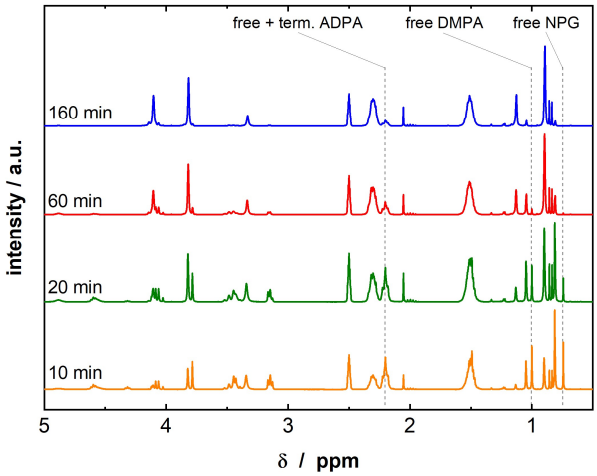

Fig.3: Time-dependent ^{1}H-NMR spectra of a three-component polyester. Dashed lines at NPG and DMPA methyl and ADPA methylene peaks, which are used for quantification of free monomers.

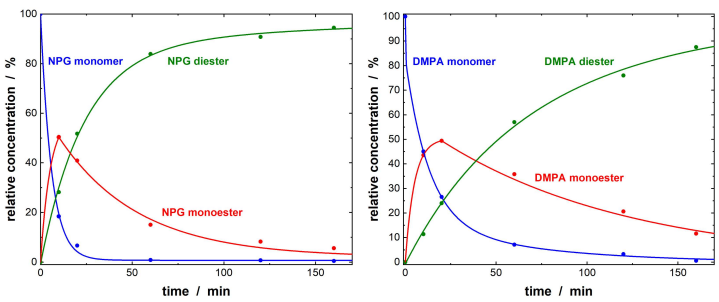

Fig.4: Concentration of neopentyl glycol (NPG) and dimethylolpropionic acid (DMPA) monomer, monoester and diester, respectively.