KIT
Karlsruhe Institute of Technology

Renewable, Pyridine Containing Polymers

Sandra Wegelin[1], Michael A. R. Meier[1,2]

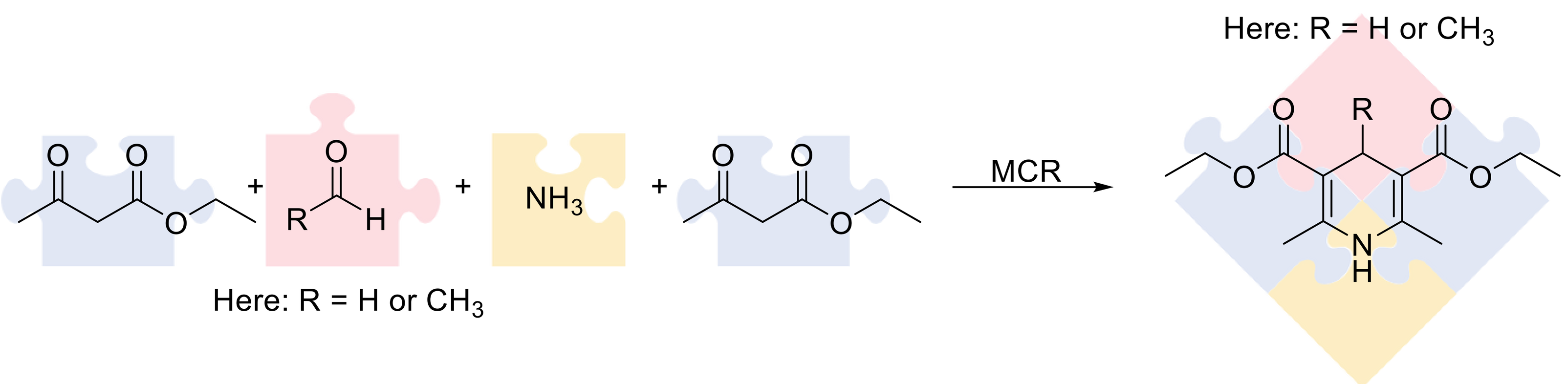
[1] Institute of Organic Chemistry (IOC), Karlsruhe Institute of Technology (KIT), Kaiserstraße 12, Karlsruhe 76131, Germany
[2] Institute of Biological and Chemical Systems – Functional Molecular Systems (IBCS-FMS), Karlsruhe Institute of Technology (KIT), Karlsruhe 76131, Germany

Abstract

Pyridine and its derivates are aromatic bases that are widely used in various applications. However, due to their great solubility in water and many organic solvents, they are hard to separate and recycle. Thus, incorporation of pyridine moieties into polymers is of considerable interest to increase their recyclability.

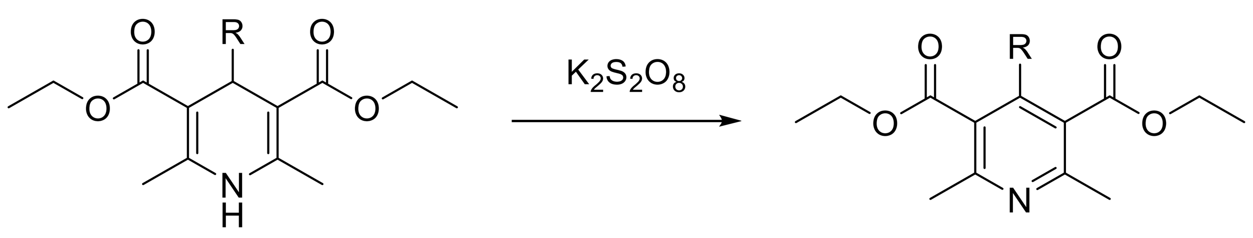
Herein, we present a new approach that incorporates the pyridine moiety directly into the polymer backbone. Monomers were prepared using the Hantzsch dihydropyridine synthesis with subsequent oxidation. For the Hantzsch reaction, only renewable starting materials were used. Oxidation of the Hantzsch dihydropyridines was performed using potassium peroxydisulfate, which is fully recyclable by electrolysis. For polymerization of the prepared monomers, two different approaches were investigated: acyclic diene metathesis and polycondensation.

1 Hantzsch DHP Synthesis



- In our case: all reactants can be produced from renewable resources
  - Ethyl acetoacetate: from renewably sourced ethyl acetate
  - Ammonia: production using renewable energy
  - Acetaldehyde: Oxidation of renewable bioethanol
  - Formaldehyde: Oxidation of renewable biomethanol

2 Oxidation



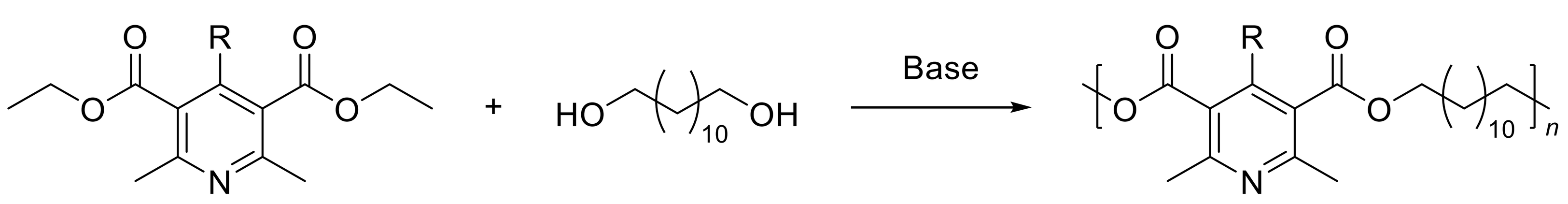
Procedure adapted from: ***Green Chem.***, 2021, **23**, 3468-3473.

$$2\ SO_4^{2-} \longrightarrow S_2O_8^{2-} + 2\ e^-$$
$$2\ H^+ + 2\ e^- \longrightarrow H_2$$

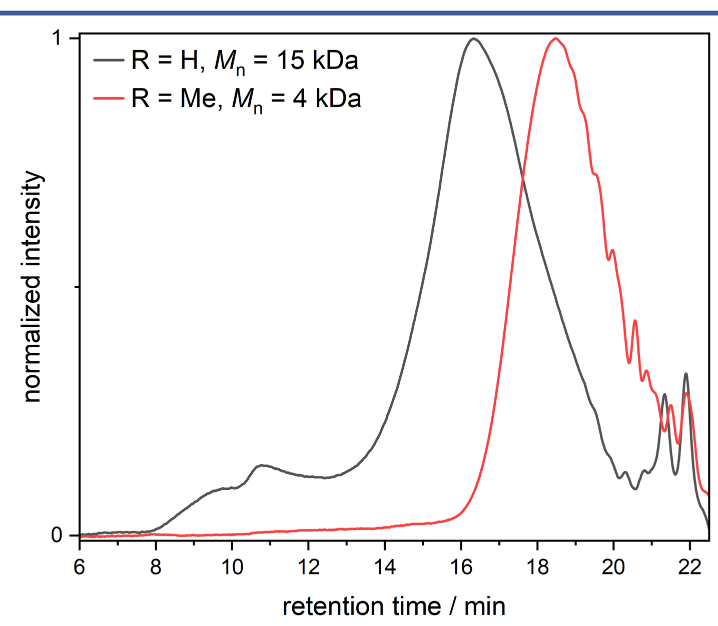
- Regeneration of peroxydisulfate anion from sulfate anion *via* electrolysis in aqueous solution

3a Polycondensation

✓ No solvent necessary ✓ Catalytic amounts of base



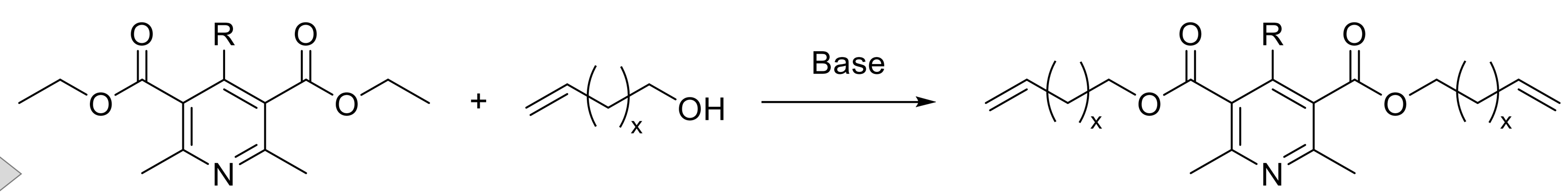
- Ethanol as volatile byproduct
- High Temperatures

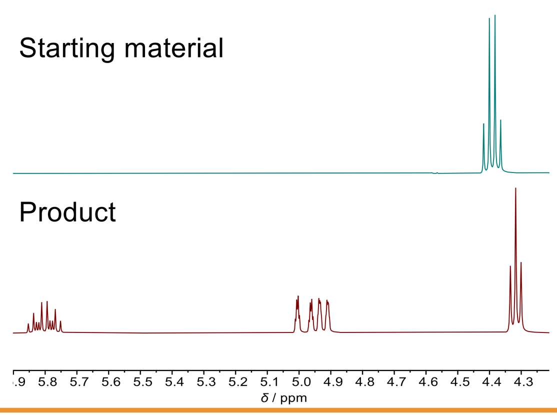


	M_n / kDa	*Đ*
R = H	15	2.4
R = Me	4	1.9

3b Transesterification

✓ No solvent necessary ✓ Catalytic amounts of base ✓ 100% conversion

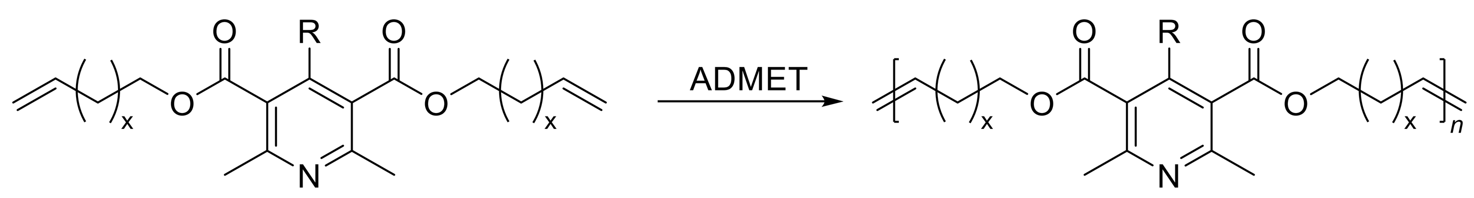


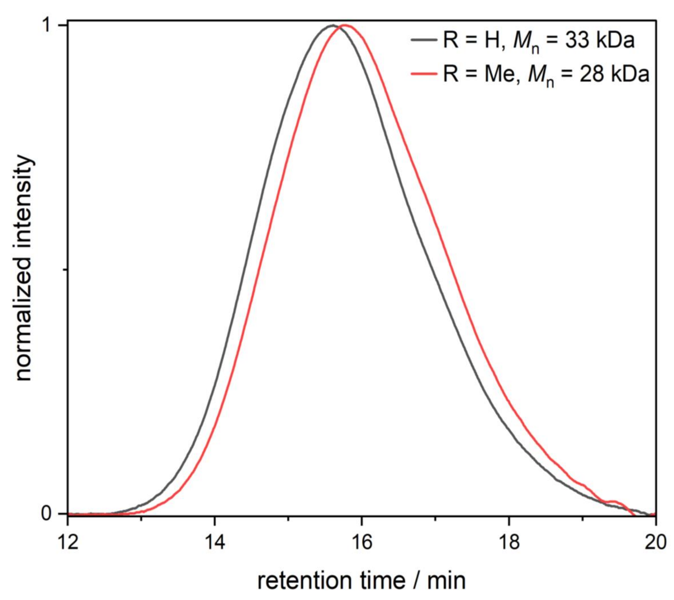


- Shift of ester neighboring CH_2 groups and change from quartet to triplet
- Characteristic signal of terminal double bonds appears

4b ADMET

✓ High efficiency ✓ Catalytic ✓ Lower temperatures





- Ethene as volatile byproduct

	M_n / kDa	*Đ*
R = H	33	1.9
R = Me	28	1.9

Contact me:

Sandra Wegelin
E-Mail: sandra.wegelin@kit.edu

My LinkedIn: Sandra Wegelin

Our group Instagram: Meier Group

Our website: Meier Group https://www.ioc.kit.edu/meier/