Enhanced Degradation and Thermal Stability in Partially Lignin-Derived Polyacetals by Incorporating a Linear Structure

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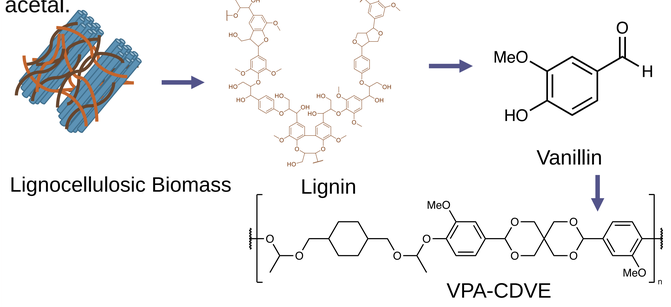
Motivation and Project Objectives

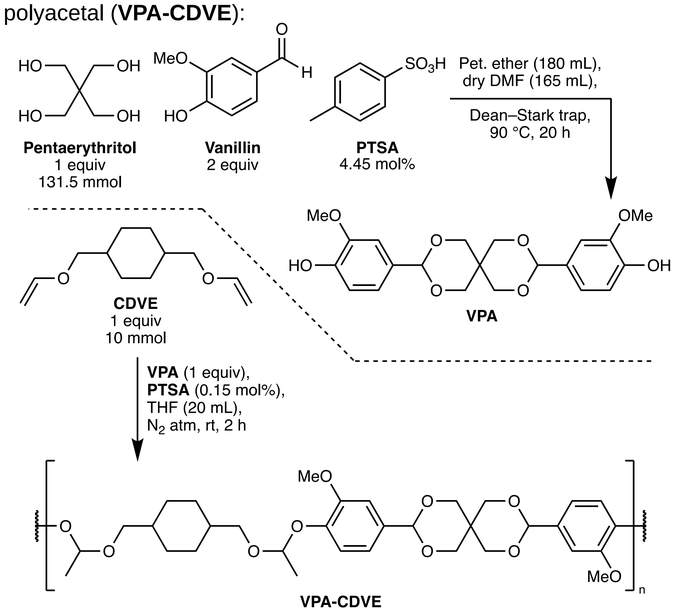
As environmental concerns grow, so does the need for sustainable polymers from renewable sources. This study tackles the urgent need to mitigate plastic pollution with polymers that effectively decompose. We are investigating a novel lignin-derived polyacetal incorporating linear acetal structures into spiro acetal frameworks. Our approach aims to enhance the polymer's degradation rate while maintaining its beneficial thermal properties. This study offers insights into the degradation behavior of this innovative polyacetal and assesses the impact of incorporating a linear acetal.



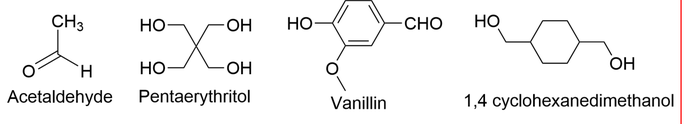
Objective: Synthesize VPA-CDVE, a vanillin-based polyacetal and asses its enhanced degradation under acidic conditions.

Polyacetal Synthesis

Synthesis of vanillin-derived monomer (**VPA**) and biodegradable polyacetal (**VPA-CDVE**):

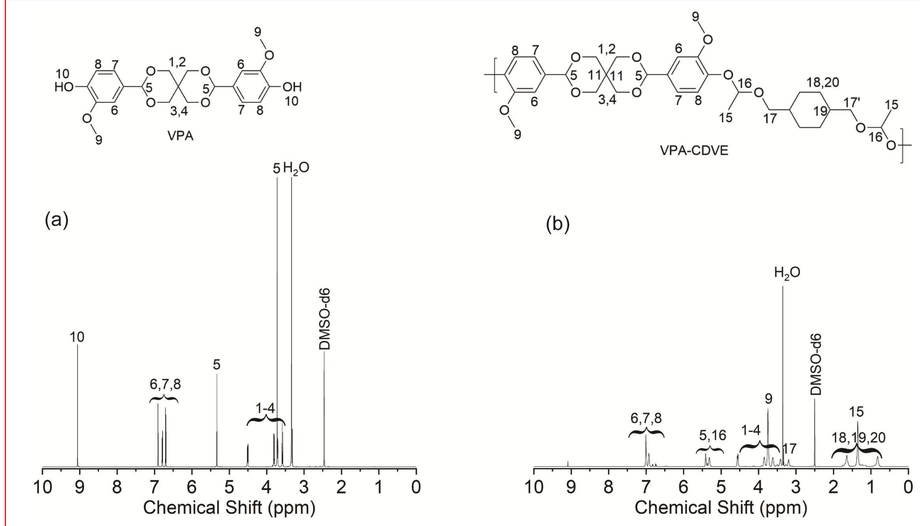


Proposed Degradation Products



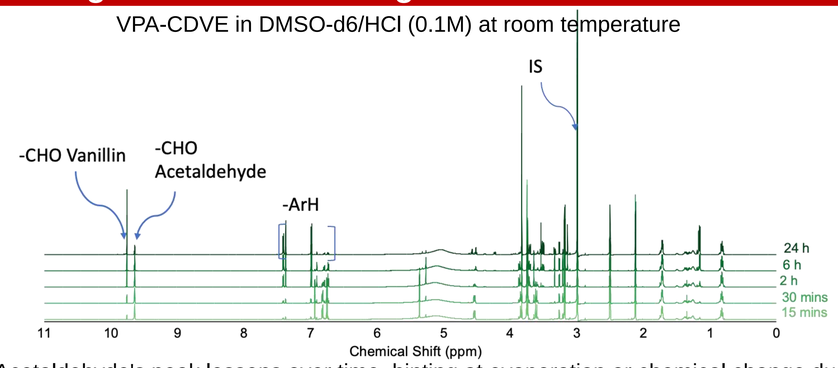
We hypothesize that the primary degradation products will be Acetaldehyde, Pentaerythritol, Vanillin and 1,4 cyclohexanedimethanol.

NMR Confirms Structure of VPA and VPA-CDVE

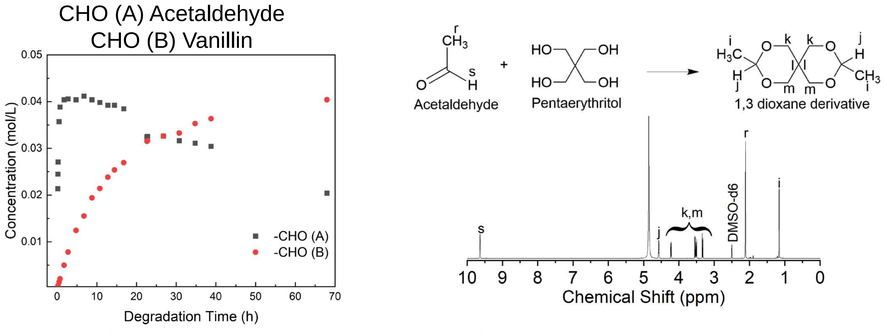


- NMR spectra conclusively verify the expected structures of VPA and VPA-CDVE.
- The chemical shifts observed in the spectra match the predicted environments for the protons within the synthesized compounds.

Degradation Monitoring of VPA-CDVE in DMSO-d6



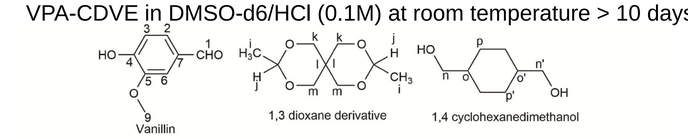
- Acetaldehyde's peak lessens over time, hinting at evaporation or chemical change due to volatility.
- The aldehyde signal of vanillin intensifies, marking its steady build-up in the reaction.

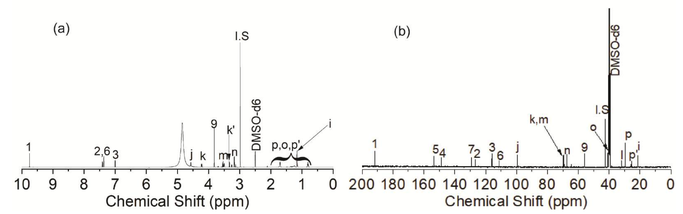


- Reaction of VPA-CDVE in DMSO-d6/HCl (0.01M).
- The linear part degrades rapidly, as indicated by the quick formation of acetaldehyde, compared to the more gradual increase of vanillin from the stable spiro part.
- Acetaldehyde concentration decreases as it reacts with pentaerythritol from the spiro part, forming a stable 1,3-dioxane derivative.

Identifying Degradation Products

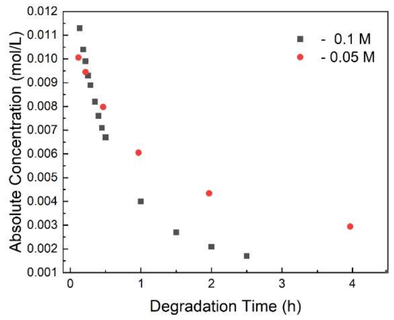
VPA-CDVE in DMSO-d6/HCl (0.1M) at room temperature > 10 days





- Identified degradation products include Vanillin, 1, 3 dioxane derivative and 1, 4 cyclohexanedimethanol.
- NMR analysis confirms that the peaks match those expected for these products.

Effect of Concentration on Degradation Kinetics



- At a higher concentration, the acid accelerates the breakdown of VPA-CDVE.
- This increase in acetal hydrolysis rate is due to the more rapid availability of protons.

Conclusions

- VPA-CDVE was synthesized and characterized, displaying stability with a Tg of 80°C and thermal degradation onset at 252°C.
- Incorporation of linear acetal units enhanced the degradation rate of VPA-CDVE, as evidenced by the direct comparison with the slower-degrading spiro part. In contrast, a previous study on VPA-DFP showed slower degradation, attributed solely to the spiro part, highlighting the beneficial impact of the linear components in VPA-CDVE.

Acknowledgements

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References

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