By-Product of the Wood Pulp Industry - Tall Oil - Utilisation for Acrylate Synthesis

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RENEWABLE RESOURCES & BIOREFINERIES

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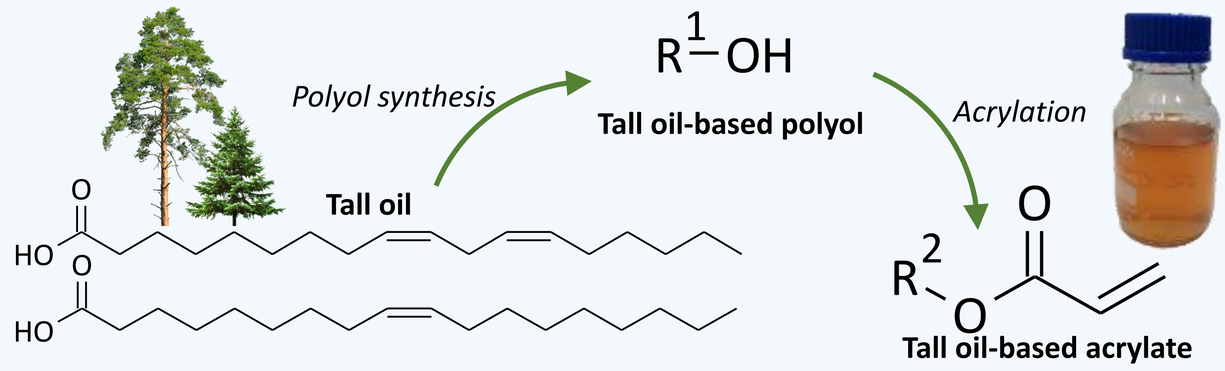
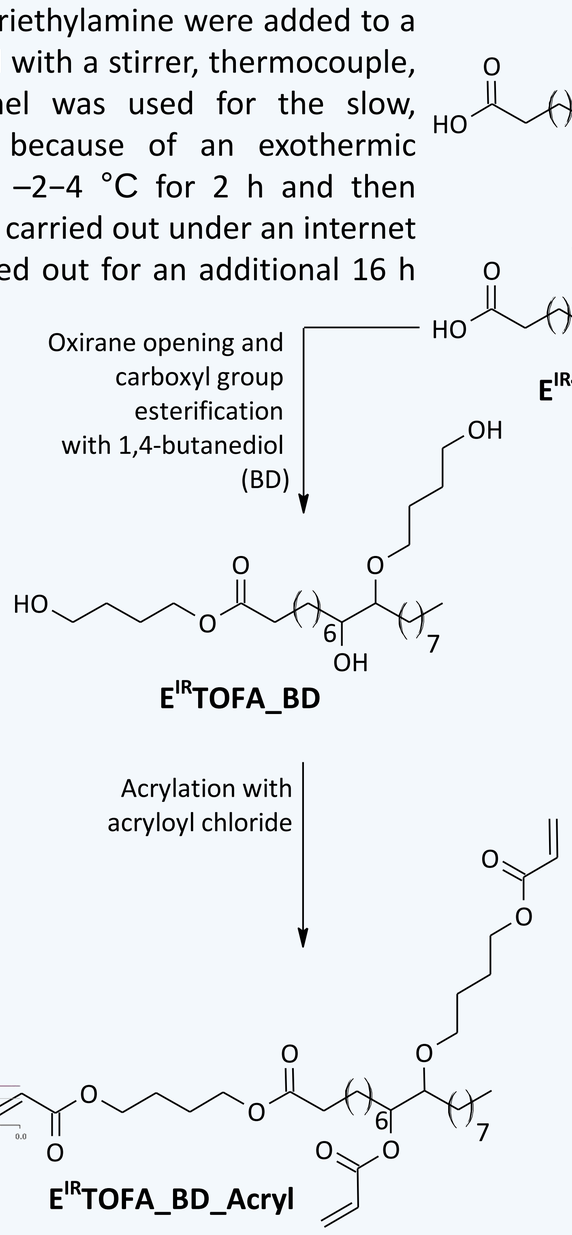
To change the existing economic climate into a greener economy, it is essential to adapt the processing of forest bio-resources into biochemicals. Distilled tall oil, a by-product of the Kraft process, mainly contains oleic and linoleic acid making it attractive for the synthesis of a variety of high-added value bio-based substances. Recently, much attention has been paid to the synthesis of multifunctional bio-based acrylates for polymer production. We report an approach for synthesising acrylates from tall oil using epoxidation, oxirane ring-opening with a polyfunctional polyol, and following hydroxyl group acrylation with acryloyl chloride.

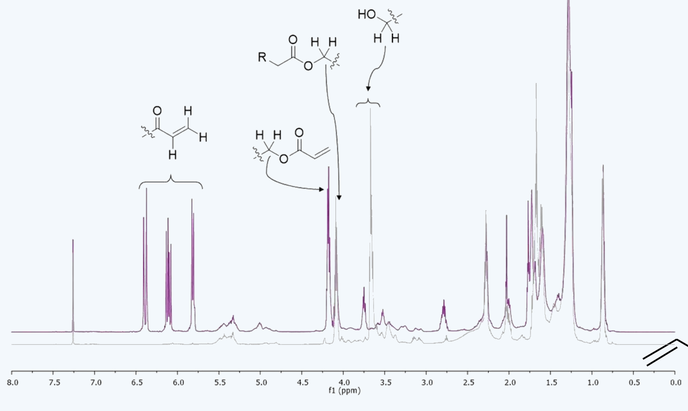


Synthesis of tall oil-based acrylate

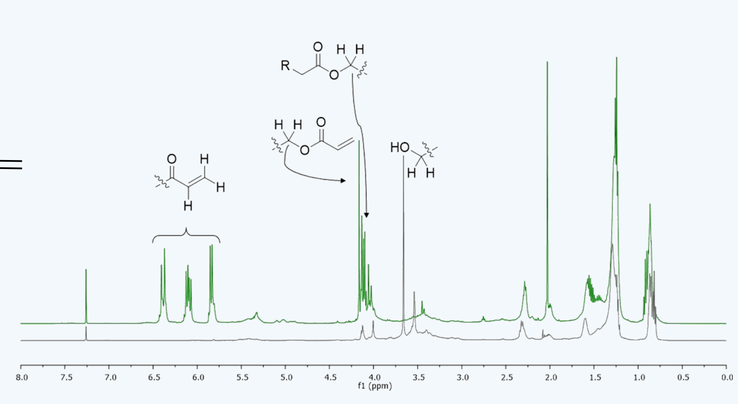
Previously synthesized polyol, E^{IR}TOFA_BD or E^{IR}TOFA_TMP, and a corresponding amount of ethyl acetate and triethylamine were added to a round bottom flask with four necks equipped with a stirrer, thermocouple, and a reflux condenser. A dropping funnel was used for the slow, intermittent pouring of acryloyl chloride because of an exothermic reaction. The temperature was maintained –2–4 °C for 2 h and then acryloyl chloride was added in. Synthesis was carried out under an internet atmosphere. Afterwards, synthesis was carried out for an additional 16 h at room temperature.

The molar ratio of polyol hydroxyl groups to acryloyl chloride was 1:1.05. The molar ratio of TEA to acryloyl chloride was 1:1. The mass ratio of polyol to ethyl acetate was 1:5. After synthesis, the mixture was filtrated.and washed with a 0.5% sodium hydroxide solution and warm distilled water and dried with anhydrous sodium sulfate. The solvent was removed using a rotary evaporator at low pressure.

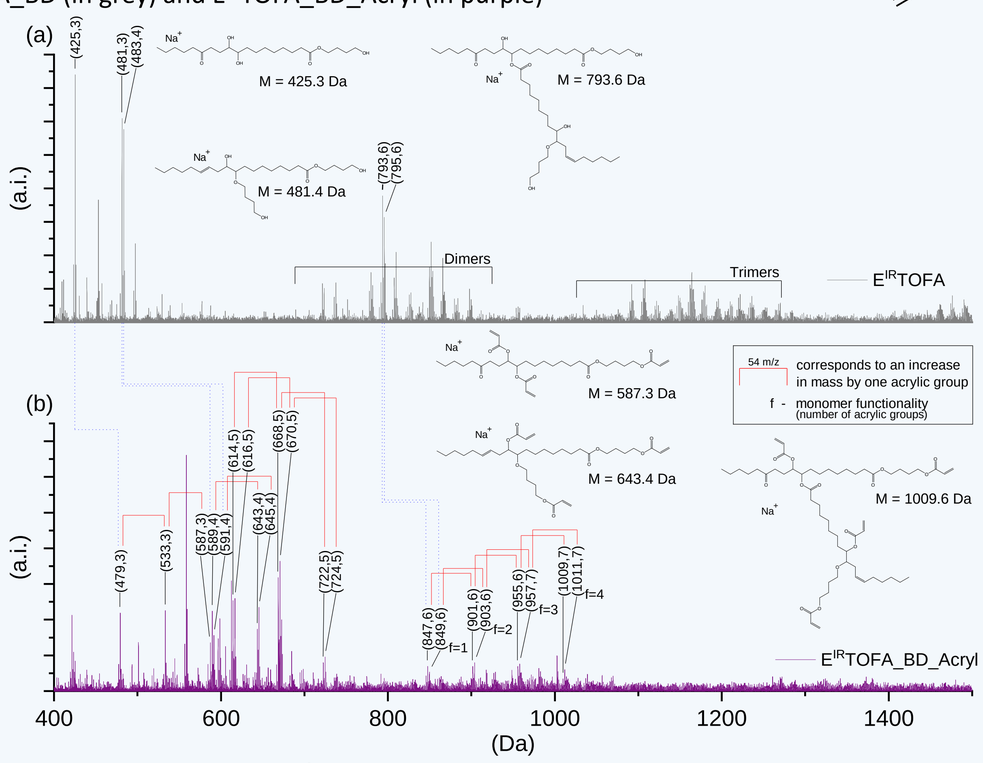




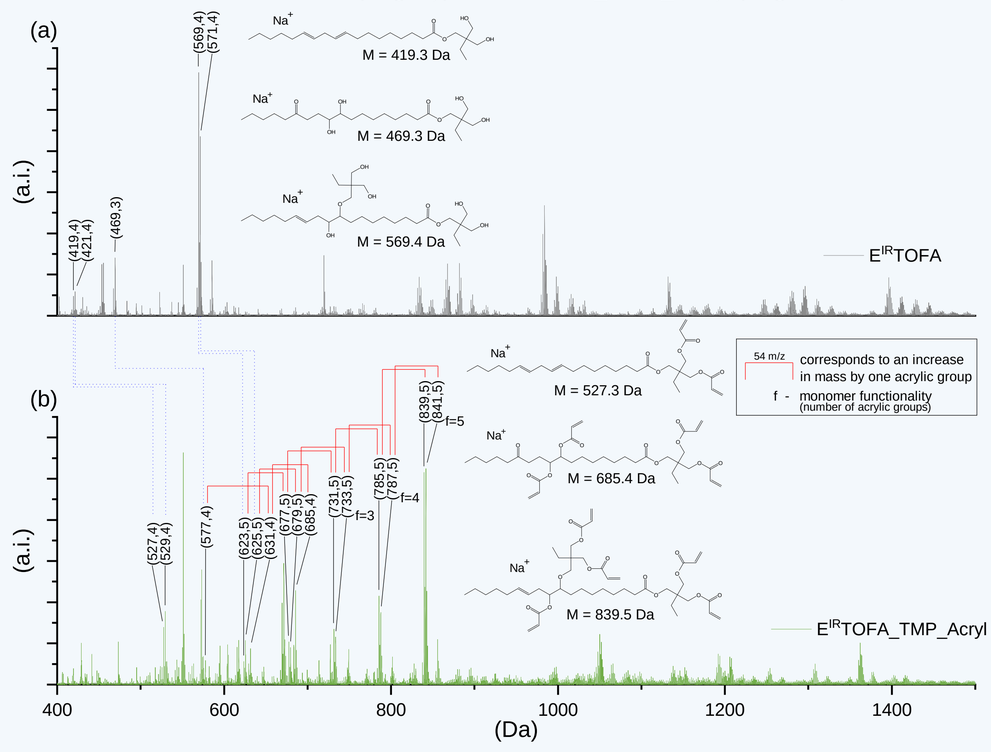
Proton nuclear magnetic resonance spectra for E^{IR}TOFA_BD (in grey) and E^{IR}TOFA_BD_Acryl (in purple)



Proton nuclear magnetic resonance spectra for E^{IR}TOFA_TMP (in grey) and E^{IR}TOFA_TMP_Acryl (in green)



Matrix-assisted laser desorption/ionization-time of flight spectra of tall oil-based polyol and tall oil-based acrylates: a) E^{IR}TOFA_BD; b) E^{IR}TOFA_BD_Acryl



Matrix-assisted laser desorption/ionization-time of flight spectra of tall oil-based polyol and tall oil-based acrylates: a) E^{IR}TOFA_TMP; b) E^{IR}TOFA_TMP_Acryl

Methods of analysis

The proton nuclear magnetic resonance (^{1}H-NMR) spectra were recorded with a Bruker spectrometer (Bruker BioSpin, Fällanden, Switzerland) at 500 and 126 MHz, respectively. Deuterated chloroform ($CDCl_3$) was used as the solvent. The ^{1}H-NMR spectra were used for the determination of acrylic group content using 1,2,3 trimethoxybenzene as an internal standard.

The matrix-assisted laser desorption/ionization-time of flight measurements were carried out using the UltrafleXtreme TOF–TOF mass spectrometer (Bruker Daltonics, Bremen, Germany) with a 2 000 Hz smartbeam-II laser (355 nm) operating in positive ion mass reflectron mode. For molecular weight assignment, panoramic pulsed ion extraction and external calibration were used.

Conclusions

Although synthesised E^{IR}TOFA-based polyols consist of a mixture of various derivatives, they contain free hydroxyl groups, which can be converted to acrylic groups. Considering the proton nuclear magnetic resonance data and Matrix-assisted laser desorption/ionization-time of flight spectra, the synthesised acrylates from tall oil fatty acids-based polyols contain several acrylic groups required for polymerisation according to the Michael reaction mechanism. E^{IR}TOFA_BD_Acryl contains 0.0039 mol/g acrylic groups, but E^{IR}TOFA_TMP_Acryl contains 0.0035 mol/g acrylic groups. The obtained tall oil polyol-based acrylates are suitable for polymer synthesis by the Michael reaction. Moreover, the synthesised tall oil polyol-based acrylates are promising in producing other polymers, for example, in UV-initiated free radical polymerisation in the production of coatings.

Acknowledgements

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