

Synthesis of AB-alternating polyacrylamides for energy applications

Maximilian Augustin, Julia Bičvič, Felix Leibetseder, and Klaus Bretterbauer

Institute for Chemical Technology of Organic Materials, Johannes Kepler University Linz, Austria

Key Points

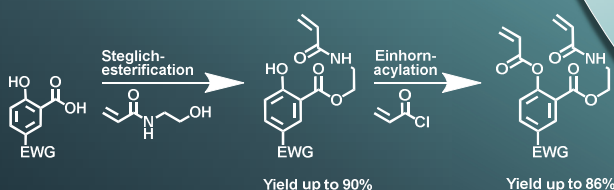
- ✓ Highly ordered AB-alternating polymer
- ✓ Unique material properties
- ✓ Tailorable architecture
- ✓ Multi-gram scalable synthesis

Background

Polyacrylamide copolymers, obtained through radical polymerization, are promising alternatives to commercially used polymers in various energy applications, like lithium-ion batteries [1]. These polymers show high potential due to their tailorable molecular architecture and functional properties, such as adhesiveness or ionic conductivity. The access to many different comonomers, either by synthesis or commercial availability, makes these polymers modifiable and purpose-built materials. The sequence of the polymer chains has a significant influence on material properties, like highly ordered alternating copolymers show better or even new anisotropic properties. With classical radical copolymerization, these highly sequenced polymers are not obtainable.

Monomer Synthesis

We have developed an improved procedure for the synthesis of different monomers used to produce AB-alternating polyacrylamides. The monomers are based on salicylic acid derivatives and two acryl groups. In comparison to published literature [2,3] no purification via column chromatography is needed, because of a new developed workup. The established scalable synthesis route enables material testing. Additionally, new derivatives were tested to further improve the synthesis, reduce production cost, influence monomer stability, solubility, and polymerization behavior.

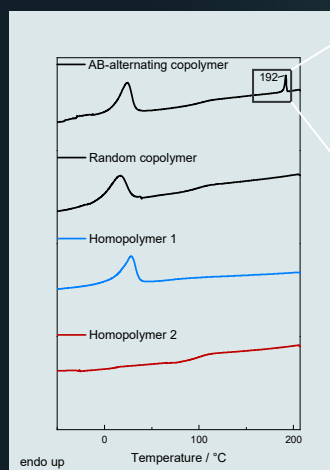
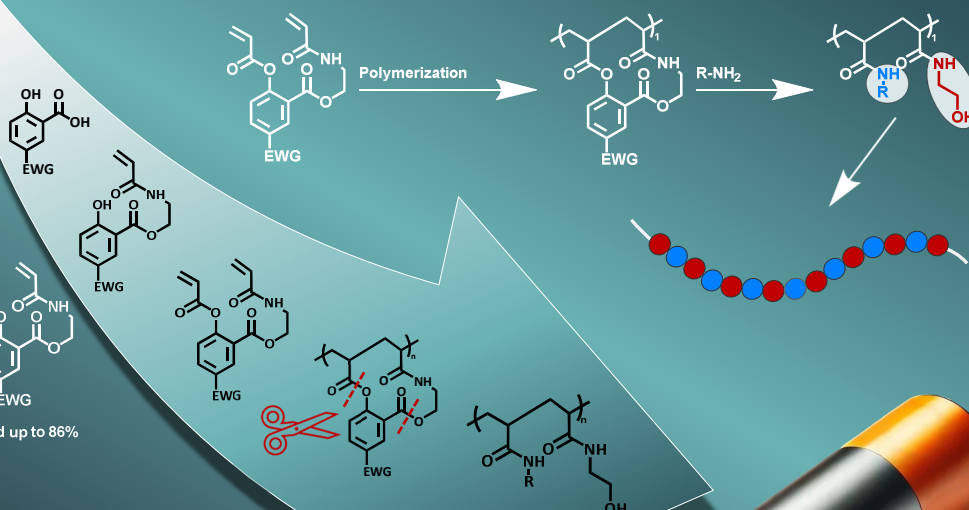


Polymerization

The produced divinyl monomer then can be polymerized either by classic free radical or with raft polymerization, in a thermally or photoinduced manner. The electron withdrawing group (EWG) dramatically influences the polymerization behavior. Initial nitro derivatives showed poor conversions and low molecular weight, leading to the use of trifluoromethyl-substituted, halogenated, nitrile-substituted, and unsubstituted divinyl monomers are under testing for polymerization and deprotection behavior. The choice of solvent and initiation are key-factors to prevent cleavage of the ester bond and loss of sequence control.

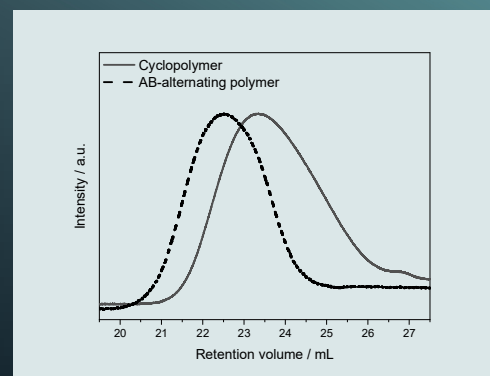
Deprotection

Tailored AB-alternating polymers for energy applications are then obtained through deprotection of the cyclopolymer with any nucleophile amine. The huge variety of usable amines offers simple production for a broad range of alternating copolymers.



The DSC thermogram on the left shows a unique property of the AB-alternating polymer. In neither of the homopolymers nor the random copolymer this signal, associated with the melting of the side chains, is found [2].

The diagram on the right shows the size exclusion chromatography results of the cyclopolymer and the AB-alternating polymer obtained from the deprotection. The change in molecular weight is corresponding to the amine used for deprotection.



[1] Leibetseder, F., Xie, J., Leeb, E., Hesser, G., Pettinger, K., & Bretterbauer, K. Recyclable Fluorine-Free Water-Borne Binders for High-Energy Lithium-Ion Battery Cathodes. *Advanced energy materials* 14, 2401074 (2024)

[2] Kametani, Y., Tournilhac, F., Sawamoto, M., & Ouchi, M. Unprecedented Sequence Control and Sequence-Driven Properties in a Series of AB-Alternating Copolymers Consisting Solely of Acrylamide Units. *Angewandte Chemie - International Edition* 59, 5193–5201 (2020)

[3] Shibata, K., Kametani, Y., Daito, Y., & Ouchi, M. Homopolymer-block-Alternating Copolymers Composed of Acrylamide Units: Design of Transformable Divinyl Monomers and Sequence-Specific Thermoresponsive Properties. *Journal of the American Chemical Society*, 144, 9959–9970 (2022)



Maximilian Augustin
Master Student
Johannes Kepler University Linz
m.augustin262@gmail.com