Universität Rostock

Traditio et Innovatio

Incorporation of Imidazolium-based Ionic Liquids in Non-isocyanate Polyurethane Networks

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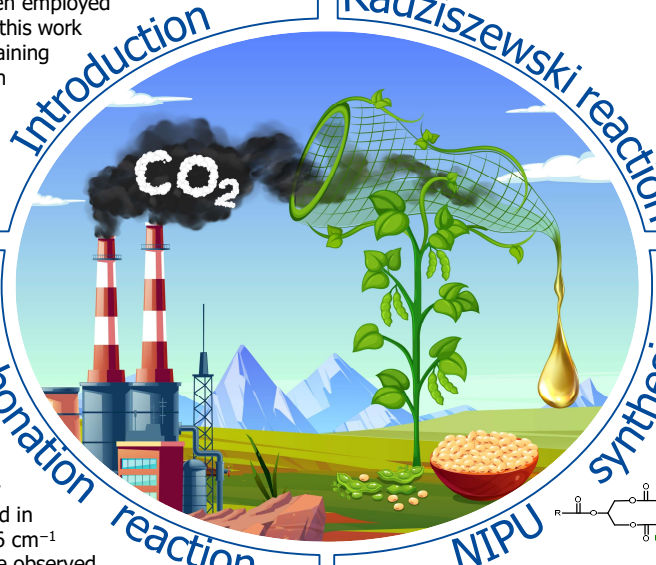
Introduction

Over the past few decades, numerous strategies to capture and reduce carbon dioxide have been widely discussed due to rising greenhouse gas emissions. Conversion of CO_2 as a nontoxic, abundant, and inexpensive resource into valuable chemicals is one of the finest routes to overcome this concern. Cyclic carbonates are one popular group of chemicals that can be prepared from the reaction of CO_2 and epoxides. Moreover, the utilization of renewable resource-based materials like vegetable oils to obtain bio-based cyclic carbonates as green substitutes for petroleum derivatives has attracted significant interest.[1] Non-isocyanate polyurethane (NIPU) products are one of their outstanding applications, which typically can be obtained by cross-linking multifunctional cyclic carbonates with amines, and they have been applied for a wide variety of purposes, including adhesives and sealants, chemical-resistance coatings, as well as biomedical applications like biodegradable scaffold and wound dressing.[2] On another hand, diverse amine compounds have been employed in the synthesis of NIPU. However, this work introduces a novel approach to obtaining NIPU networks through the reaction of cyclic carbonate and amino-terminated poly imidazolium-based ionic liquids derived via the multicomponent poly-Radziszewski reaction.



Radziszewski reaction

Two series of main-chain imidazolium-containing polymeric ionic liquids (PILs) were synthesized by means of the multicomponent poly-Radziszewski reaction (Fig. 3).[4] Accordingly, 1,4-butanediamine and 1,6-hexanediamine were employed as precursors with different amine/carbonyl molar ratios to produce PIMC4 and PIMC6 compounds, respectively. The formation of imidazolium moieties in the backbone of PILs was confirmed by ATR-FTIR and NMR spectroscopies. In addition, the molecular weight distributions of synthesized PILs were investigated by aqueous GPC and are provided in Table 2.

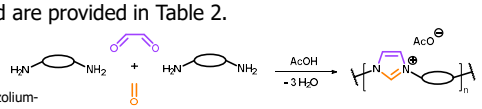


Fig. 3: Synthesis of imidazolium-containing PIL's through the poly-Radziszewski reaction.

Table 2: Molecular weight distributions of PIM's synthesized by varying the amine/carbonyl molar ratio in the monomer feed.

Molar ratio	Mn	Mw	PDI
PIMC4-0.8	27245	276540	10.15
PIMC4-1.2	7982	17007	2.10
PIMC4-1.6	5799	9167	1.58
PIMC4-2.0	5057	7805	1.54
PIMC6-0.8	19862	223260	11.24
PIMC6-1.2	8387	18018	2.14
PIMC6-1.6	6114	10344	1.69
PIMC6-2.0	5695	8680	1.52

Carbonation reaction

Cyclic carbonated soybean oil (CSBO) was prepared by CO_2 fixation into epoxidized soybean oil (ESBO) at 110 °C for 70 h under a TBAB/$CaCl_2$ catalytic system (Fig. 1).[3] The cycloaddition reaction was tracked by ATR-FTIR and NMR spectroscopies, as well as GPC, viscosity measurements, and epoxy content determination. As presented in Fig. 2, new peaks at 1048 and 1796 cm^{-1} related to carbonate formation were observed and increased in intensity. Oppositely, the disappearance of the oxirane C-O twin bands at 845 cm^{-1} approved the consumption of epoxide groups. Besides, the incorporation of CO_2 into the epoxy group led to a slight and continuous rise in the molecular weight of carbonated oils, while rheological analysis revealed a significant increase in product viscosity (Table 1).

Table 1: Molecular weight and viscosity of CSBO at different reaction times.

Duration (h)	M_w (g/mol)	η (Pa-s)
0	1516	0.4067
23	1587	4.6273
46	1654	10.0387
70	1740	16.8693

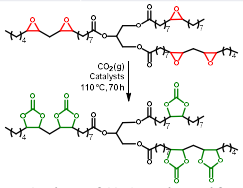


Fig. 1: Synthesis of CSBO via chemical fixation of CO_2 into ESBO.

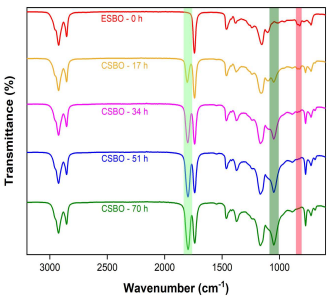


Fig. 2: FT-IR spectra of carbonated soybean oil at different reaction times.

NIPU synthesis

In order to synthesis NIPU compounds, CSBO was cured with PILs by a step-growth polymerization reaction. This reaction was performed in a three-neck flask with an inlet for argon and a condenser.

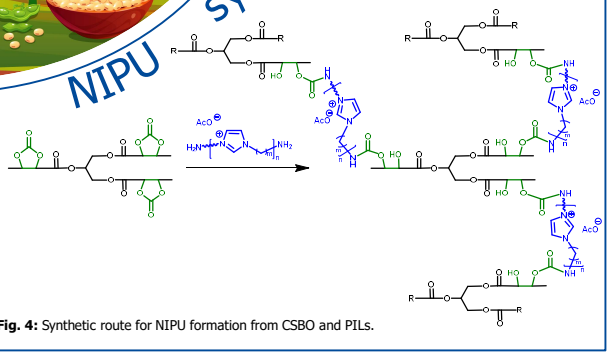


Fig. 4: Synthetic route for NIPU formation from CSBO and PILs.

Summary and outlook

- ✓ Successful synthesis of carbonated vegetable oil under low pressure of CO_2
- ✓ Successful synthesis of polymeric ionic liquids with different lengths of alkyl chain

Further works:

- ❑ Swelling characterization
- ❑ Mechanical investigation
- ❑ Biocompatibility test

References

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