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. Bio-based cyclic carbonates are one popular group of chemicals that can be prepared from the reaction of CO_2 and renewable resource-based epoxides. **Non-isocyanate polyurethane (NIPU)** products are one of their outstanding applications, which typically can be obtained by cross-linking multifunctional cyclic carbonates with amines.[1] Herein, we introduce a novel approach to prepare NIPU networks through the reaction of bio-based cyclic carbonates and amino-terminated poly imidazolium-based ionic liquids derived by means of the multicomponent **poly-Radziszewski** reaction.

CO_2 utilization

Cyclic carbonated soybean oil (CSBO) was prepared by incorporation of CO_2 into epoxidized soybean oil (ESBO) under a TBAB/$CaCl_2$ catalytic system (Fig. 1).[2] The cycloaddition reaction was tracked and approved by FT-IR and NMR spectroscopies, as well as GPC, viscosity measurements, ESI-MS, and epoxy content determination.

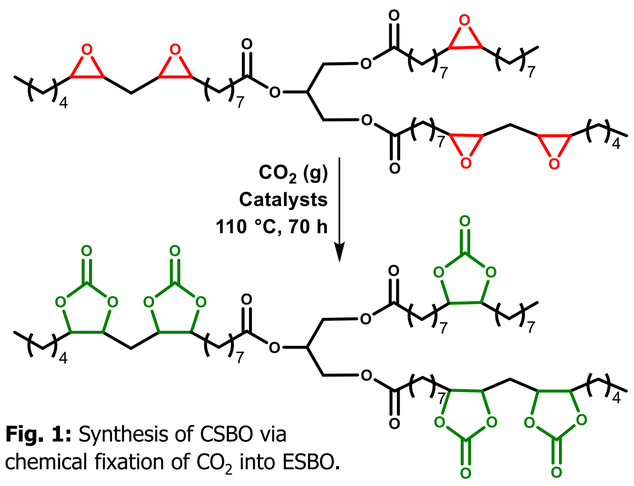
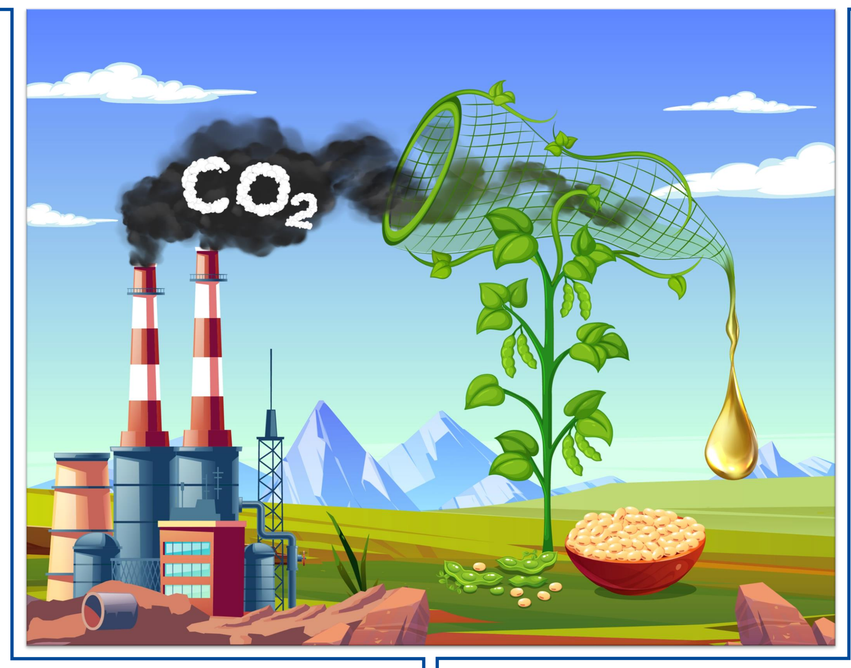


Fig. 1: Synthesis of CSBO via chemical fixation of CO_2 into ESBO.



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

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

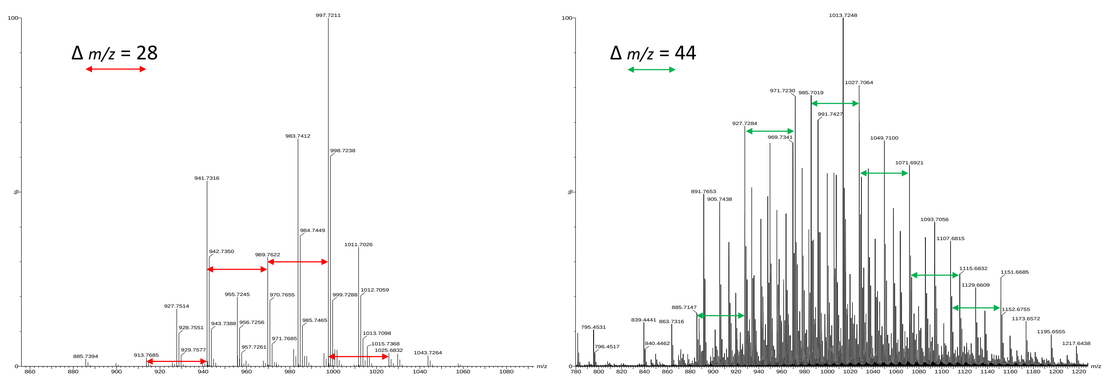


Fig. 2: ESI-MS spectra recorded for ESBO (left) and CSBO (right).

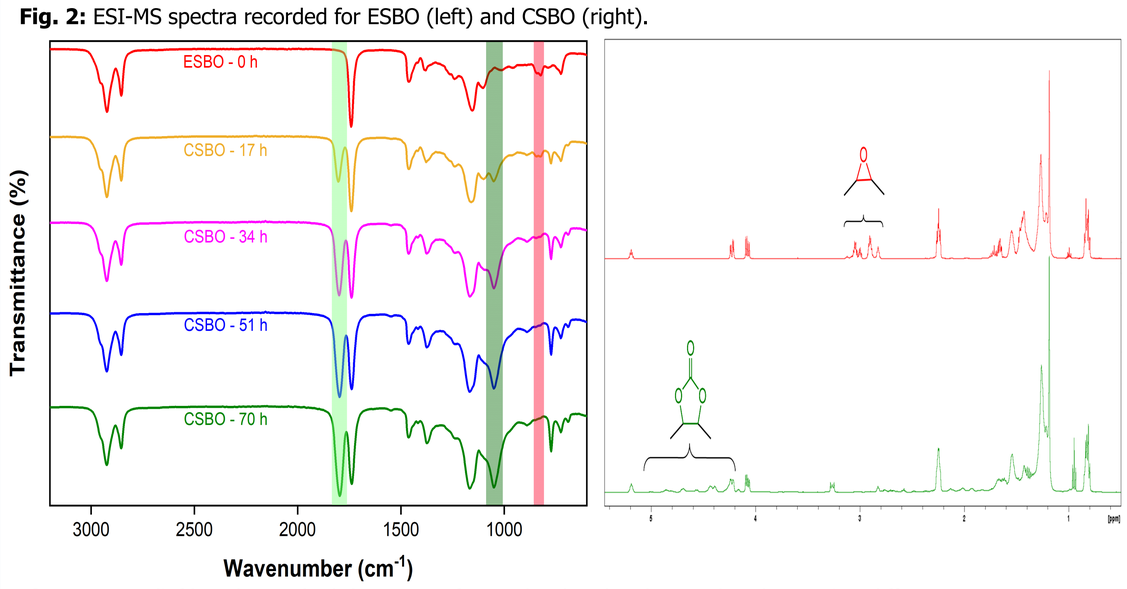


Fig. 3: FT-IR (left) and NMR (right) spectra of epoxidized and carbonated soybean oil at different reaction times.

Poly(IL)s preparation

Two series of **imidazolium-containing polymeric ionic liquids (PILs)** were synthesized via the poly-Radziszewski reaction (Fig. 4).[3] Accordingly, 1,4-butanediamine and 1,6-hexanediamine were employed as precursors with different amine/carbonyl molar ratios to produce PIMC4 and PIMC6 compounds. The formation of imidazolium moieties was confirmed by FT-IR as well as NMR spectroscopies, and the molecular weight distributions of synthesized PILs were investigated by GPC (Table 2).

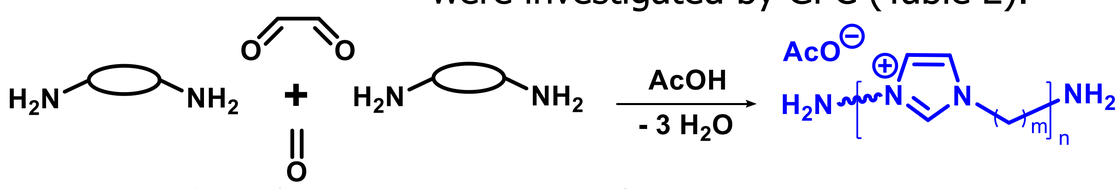


Fig. 4: Synthesis of imidazolium-containing PIL's through the poly-Radziszewski reaction.

	Molar ratio	Mn	Mw	PDI
PIMC4	0.8	27240	276540	10.15
	1.0	13440	39580	2.94
	1.2	7980	17000	2.1
	1.4	6580	12590	1.91
	1.6	5800	9170	1.58
	1.8	5400	8410	1.55
	2.0	5060	7800	1.54
	2.2	4760	7380	1.54

	Molar ratio	Mn	Mw	PDI
PIMC6	0.8	19860	223260	11.24
	1.0	14725	73400	4.98
	1.2	8390	18010	2.14
	1.4	7065	12600	1.78
	1.6	6114	10345	1.69
	1.8	5610	8710	1.55
	2.0	5695	8680	1.52
	2.2	5320	8260	1.55

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

NIPU synthesis

In order to synthesis NIPU compounds, CSBO was cured with PILs by a step-growth polymerization reaction.

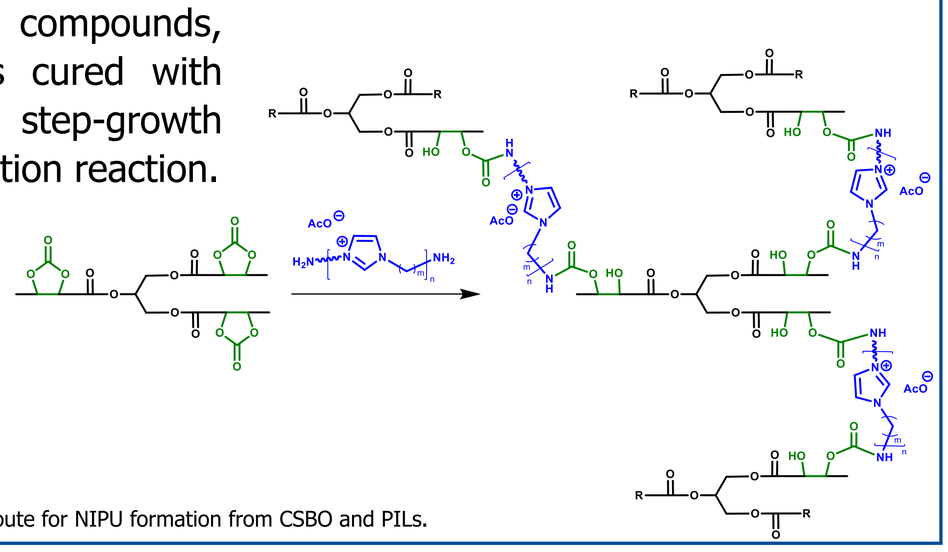


Fig. 5: Synthetic route for NIPU formation from CSBO and PILs.

References

[1] M. Bähr and R. Mülhaupt, *Green Chemistry* **2012**, 14, 483-489.

[2] H. Gholami and H. Yeganeh, *Biomedical Materials* **2020**, 15, 045001.

[3] J.-P. Lindner, *Macromolecules* **2016**, 49, 2046-2053.

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