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## LINKING CELLULOSE CHAINS USING DIBROMOALKANES IN THE DMSO/DBU/CO<sub>2</sub> SWITCHABLE SOLVENT SYSTEM

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Abstract - The depletion of fossil resources has prompted both academia and industry to pursue more sustainable alternatives, particularly in the field of polymer science. Among these, cellulose – the most abundant natural macromolecule on Earth - has attracted considerable interest. While various products and processes have been developed through the physical and chemical modification of solid-state cellulose, the dissolution of cellulose has emerged as a key strategy for producing more homogeneous materials and enabling novel chemical transformations. In 2005, Jessop and co-workers introduced the DMSO/DBU/CO<sub>2</sub> solvent system for organic synthesis [1]. This system, composed of a non-ionic liquid mixture of an alcohol and an amine base, transforms into an ionic liquid upon exposure to carbon dioxide. More recently, this solvent system has been adapted for cellulose dissolution, yielding homogeneous solutions and allowing chemical modifications under milder conditions [2-5]. However, the use of bifunctional reagents for cellulose modification in this solvent system remains largely unexplored. Such reagents can induce crosslinking reactions between dissolved cellulose chains, leading to the formation of macromolecular networks with properties that depend on the degree of crosslinking and the reagent employed. In this context, the present study investigated the reaction of cellulose with 1,4dibromobutane and 1,12-dibromododecane using varying cellulose/substrate ratios. Successful chemical modification was confirmed by infrared spectroscopy – through the appearance of a carbonate ester C=O symmetric stretching band at 1740 cm<sup>-1</sup> – and X-ray diffraction, which showed the disappearance of cellulose's characteristic crystalline pattern. Gel formation during these reactions provided further evidence of crosslinking between cellulose chains. The extent of crosslinking was estimated through water swelling experiments, with one sample exhibiting a mass increase of up to 1340%.

## References

- **1.** P. G. Jessop; D. J. Heldebrant; X. Li; C. A. Eckert; C. L. Liotta, *Nature*, 2005, 436, 7054, 1102-1102. https://doi.org/10.1038/4361102a.
- **2.** K. N. Onwukamike, S. Grelier, E. Grau, H. Cramail, M. A. R. Meier, *ACS Sustainable Chem. Eng.* 2018, 6 (7), 8826–8835. https://doi.org/10.1021/acssuschemeng.8b01186.
- **3.** K. N. Onwukamike, T. Tassaing, S. Grelier, E. Grau, H. Cramail, M. A. R. Meier, *ACS Sustainable Chem. Eng.* 2018, 6(1), 1496–1503. https://doi.org/10.1021/acssuschemeng.7b04053.
- 4. J. Wolfs, M. A. R. Meier, Green Chem. 2021, 23 (12), 4410–4420. https://doi.org/10.1039/D1GC01508G.
- **5.** J. Wolfs, R. Nickisch, L. Wanner, M. A. R. Meier, *J. Am. Chem. Soc.* 2021, 143 (44), 18693–18702. https://doi.org/10.1021/jacs.1c08783.

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