Dual Ionic Liquid-Functionalized Cellulosic Materials: Thermal, Mechanical and Conductive Properties

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ABSTRACT

Cellulose, an inexpensive and renewable biomacromolecule, represents an intriguing synthetic foundation for new materials with task-specific properties. Here, we wish to report a synthetic route for functionalizing cellulose with a side chain containing two ionic liquid functional groups using azide-alkyne ‘click’ cyclization strategy, followed by quaternization of the two resulting heterocycles (1,2,3-triazole and imidazole). Through this functionalization strategy, the resulting cellulosic materials exhibited significant softening, with several glass transition (Tg) values observed below room temperature, indicating the amorphous nature of the materials, with the Tg dependent on both the length of the side chain and the counteranion used. Stress and strain at break of the materials were found by dynamic mechanical analysis to generally be in excess of 2 MPa and 250 %, respectively, indicating not only a high degree of mechanical robustness, but also elastomeric. Enhancements in conductivity as high as 6 orders of magnitude were found when compared to native cellulose. In the end, cellulose can be utilized as a sustainable, foundational biopolymer in the preparation of new conductive materials.

INTRODUCTION

- Structural saccharide polymers, such as cellulose, interact through hydrophobic and electrostatic interactions, and the resulting matrices can exhibit useful and novel properties.
- First-generation IL-functionalized cellulosic materials utilized azide-alkyne click cyclization, followed by quaternization, to create 1,2,3-triazole groups off of each sugar unit.
- The presence of the 1,2,3-triazole group led to a 6-orders of magnitude enhancement in conductivity versus microcrystalline cellulose, with Tg values of approximately 100 °C, however, the materials lacked flexibility.

SYNTHESIS

Synthesis of Alkynyl-Substituted Imidazoles


FUNCTIONALIZATION OF CELLULOSE

- Structural saccharide polymers, such as cellulose, interact through hydrophobic and electrostatic interactions, and the resulting matrices can exhibit useful and novel properties.
- First-generation IL-functionalized cellulosic materials utilized azide-alkyne click cyclization, followed by quaternization, to create 1,2,3-triazole groups off of each sugar unit.
- The presence of the 1,2,3-triazole group led to a 6-orders of magnitude enhancement in conductivity versus microcrystalline cellulose, with Tg values of approximately 100 °C, however, the materials lacked flexibility.

ANALYSES

Mechanical (DMA) Stress-Strain Data

- Stress and strain at break were found to be in excess of 2 MPa and 250 %, respectively, indicating not only a high degree of mechanical robustness, but also elastomeric.
- Enhancements in conductivity as high as 6 orders of magnitude were found when compared to native cellulose. In the end, cellulose can be utilized as a sustainable, foundational biopolymer in the preparation of new conductive materials.

SUMMARY

- Cellulose is an inexpensive and sustainable raw material which, when functionalized with an ionic liquid unit, could serve as an important foundational polymer for new PILs.
- Functionalization of cellulose leads to a disruption of hydrogen bonding, an increase in free volume and segmental motion, leading to a decrease in Tg and an increase in ionic conductivity.
- The additional IL (imidazolium) unit further decreased Tg while increasing flexibility and conductivity.


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