UNIVERSITI TEKNOLOGI MARA

PROTON CONDUCTING AND LIGHT-RESPONSIVE LIQUID CRYSTAL POLYMERS FOR MULTIFUNCTIONAL POLYMER ELECTROLYTES

SAKINAH MOHD ALAUDDIN

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AUTHOR'S DECLARATION

I declare that the work in this thesis was carried out in accordance with the regulations of Universiti Teknologi MARA. It is original and is the results of my own work, unless otherwise indicated or acknowledged as referenced work. This thesis has not been submitted to any other academic institution or non-academic institution for any degree or qualification.

I, hereby, acknowledge that I have been supplied with the Academic Rules and Regulations for Post Graduate, Universiti Teknologi MARA, regulating the conduct of my study and research.

Name of Student	:	Sakinah binti Mohd Alauddin
Student I.D. No.	:	2014822034
Programme	:	Doctor of Philosophy in Chemical Engineering - EH950
Faculty	:	Chemical Engineering
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Signature of Student	:	………………………………………………..
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ABSTRACT

Electrochemical devices are gaining attention as an enabling technology for renewable energy, energy harvesting, storage and decarbonization. Nevertheless, a crucial part of this device, the electrolyte, still requires design enhancement to facilitate efficient proton transport and thus elevate device efficiency. Therefore, the objective of this work is to synthesize new electrolytes with enhanced proton conductivity. The synthesized electrolytes were tailored with multifunctional liquid crystalline materials containing light-responsive mesogenic groups (MeOAzB), polar sulfonic acids (AMPS), and methyl(methacrylate) groups (MMA) via different polymerization techniques, block and statistical copolymerization; side-chain lengths; and mesogen terminal groups. These liquid crystal polymers (LCP) were characterized by their chemical structure, thermal stability, phase behaviour and structure, light-responsiveness, conductivity, and dielectric performance. All polymers displayed considerably high thermal stabilities under inert conditions making them suitable for usage in high temperature fuel cell. They were also light-responsive, *via* the reversible *trans*-to-*cis* photoisomerization of azobenzene groups in MeOAzB, which can manipulate nanoscale alignment and further promote proton conduction. These properties depended on the mesogen's terminal group, where polar (-NO2) groups showed higher thermal stability and faster relaxation. Narrow segregated proton conducting channels were formed in the block copolymerization method whereas in statistical copolymerization channels were created from aggregates in the LCP that were constrained between mesogenic/smectic layers. LCP required >30% MeOAzB to yield smectic and/or nematic phase liquid crystalline behaviour which, together with the established domain structure, provide appreciable proton conductivity in polymers. The LCP with six carbon side-chain, 6-MeOAzB/AMPS/MMA exhibited the highest conductivity of (~$10^{-2.9}$ S·cm^{-1}) in a broad range of temperatures with an electrochemical band gap 2.00 ev. This shows that phase structure could assist hole conductivity in liquid crystalline electrolytes by reducing the gap between molecular energy levels The dielectric studies and activation of these conductivities indicate that the proton mobility is activated by local molecular motions near the polymeric backbone in the AMPS-rich regions, and potentially follows ion-hopping mechanisms. The conductivity values obtained in this work are within the highest observed under anhydrous conditions for liquid crystalline materials, and not far from the results obtained for hydrated perfluorinated benchmark membranes used in commercial fuel cells, such as Nafion (0.1 S·cm^{-1}). The proton conducting channels generated by mesogenic groups and light-responsiveness of these polymers, together with the local activation of conductivity at relatively low temperatures, open the possibility to prepare new polymer electrolytes for energy conversion and storage, whose conductivity could be controlled and optimized by external stimuli of light irradiation.

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