A SYSTEMATIC STUDY ON BENZIMIDAZOLE DERIVATIVES: INVESTIGATION OF HYDROGEN BOND, PACKING STRUCTURE, AND MOLECULAR MOBILITY RELATED TO PROTON TRANSFER IN ANHYDROUS SYSTEM OF POLYMER ELECTROLYTE MEMBRANE FUEL CELL

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ABSTRACT

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The present work aims to clarify how proton can be transferred in heterocycle molecules under anhydrous system based on benzimidazole model compounds and model polymer via a simple molecular design and synthesis approach. In the case of benzimidazole model compounds, the number of benzimidazole groups under monofunctional, difunctional, and trifunctional leads us to an understanding that the hydrogen bond network among benzimidazole as well as the packing structure is the key factor for enhancing proton transfer efficiency. The most favorable structure is trifunctional benzimidazoles which gives a helical hydrogen bond network under columnar packing structure of which the conductivity is as high as 10^{-2} S/cm^2 at 170 °C. In the case of model polymer containing multifunctional benzimidazole, a branching benzimidazole polymer can be easily obtained by simply conjugating benzimidazoles onto branching polyethylenimine. This model polymer suggests that although benzimidazoles form the hydrogen bond network, the tight and strong network obstructs the chain mobility. The favorable condition for polymer containing benzimidazoles is the one with only a few percent of benzimidazole group (~20%) and at that time the conductivity is 10^{-4} S/cm^2 at 190 °C. The work also extends to show an approach to obtain branching benzimidazole pendant group which will be useful for the conjugation onto polymer backbone in the

next step. The pendant group of aminotris[2-(benzimidazol-2-yl)ethyl]methane is successfully prepared by the reaction between triacid chloride of nitromethanetripropionic acid chloride and diamine of phenylenediamine followed by the reduction of nitro group via Pd/C catalyst.

บทคัดย่อ

อัจฉรา แป้งอ่อน : การพิสูจน์ทราบของพันธะไฮโดรเจน โครงสร้างการจัดเรียงตัว และการเคลื่อนที่เชิงโมเลกุล ที่เกี่ยวกับการส่งผ่านโปรตอนในระบบที่ไม่ใช้น้ำของเซลล์เชื้อเพลิงแบบพอลิเมอร์อิเลคโตรไลท์เมมเบรน (Investigation of Hydrogen Bond, Packing Structure, and Molecular Mobility related to Proton Transfer in Anhydrous System of Polymer Electrolyte Membrane Fuel Cell) อ. ที่ปรึกษา : ศาสตราจารย์ ดร. สุวบุญ จิรชาญชัย และ ศาสตราจารย์ ดร.โคจิ ทาชิโระ, 91 หน้า

งานวิจัยนี้มุ่งเน้นให้เห็นชัดเจนถึงการส่งผ่านโปรตอนในโมเลกุลเฮเทอโรไซเคิลภายใต้ระบบที่ไม่ใช้น้ำของสารต้นแบบและพอลิเมอร์ต้นแบบของเบนซิมิดาโซล โดยวิธีออกแบบและสังเคราะห์โมเลกุลอย่างง่าย จำนวนหมู่เบนซิมิดาโซลภายใต้ หมู่ฟังก์ชันเดี่ยว หมู่ฟังก์ชันคู่ และหมู่ฟังก์ชันสาม นำมาสู่ความเข้าใจที่ว่า ร่างแหของพันธะไฮโดรเจนในหมู่เบนซิมิดาโซลรวมถึงโครงสร้างการจัดเรียงตัวเป็นปัจจัยสำคัญในการเพิ่มประสิทธิภาพการส่งผ่านโปรตอน โครงสร้างที่เอื้อต่อการส่งผ่านโปรตอนมากที่สุดคือ เบนซิมิดาโซลหมู่ฟังก์ชันสาม ซึ่งให้ร่างแหของพันธะไฮโดรเจนแบบเกลียวภายใต้โครงสร้างการจัดเรียงตัวแบบแนวตรง ที่ซึ่งค่าการนำโปรตอนเท่ากับ 10^{-2} S/cm ที่อุณหภูมิ 170 องศาเซลเซียส ในกรณีของพอลิเมอร์ต้นแบบที่ประกอบด้วยเบนซิมิดาโซลจำนวนมาก นั่นคือเบนซิมิดาโซลที่มีลักษณะเป็นกิ่ง สามารถเตรียมได้อย่างง่ายโดยการติดเบนซิมิดาโซลบนพอลีเอทธิลลีนอิมมีนที่เป็นกิ่ง พอลิเมอร์ต้นแบบนี้ชี้ให้เห็นว่า แม้ว่าเบนซิมิดาโซลจะทำให้เกิดร่างแหของพันธะไฮโดรเจน ร่างแหที่แข็งแรงและอยู่กันอย่างแน่นจะขัดขวางการเคลื่อนที่ของสายโซ่ เงื่อนไขที่เหมาะสมสำหรับพอลิเมอร์ที่ประกอบด้วยเบนซิมิดาโซลคือพอลิเมอร์ที่มีเบนซิมิดาโซลจำนวนหนึ่ง (~20%) และในขณะนั้นให้ค่าการนำโปรตอนเท่ากับ 10^{-4} S/cm ที่อุณหภูมิ 190 องศาเซลเซียส งานนี้ขยายไปสู่การแสดงวิธีได้มาซึ่งหมู่แขวนเบนซิมิดาโซลที่มีลักษณะเป็นกิ่ง ซึ่งจะมีประโยชน์สำหรับการเชื่อมติดบนสายโซ่หลักของพอลิเมอร์ในขั้นตอนต่อไป หมู่แขวนของ ทริส[2-(เบนซิมิดาโซ-2-อิว)เอททิล]ไนโตรมีเทน ถูกเตรียมได้สำเร็จจากปฏิกิริยาระหว่าง ไตรแอซิดตลอไรด์ของไนโตรมีเทนไตรโพรไพโอนิค แอซิด คลอไรด์ และไดเอมีนของฟีนิลลีนไดเอมีน ตามด้วยการรีดักชันของหมู่ไนโตรด้วยตัวเร่งปฏิกิริยา แพดลาเดียม/คาร์บอน

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