吡咯基聚方酸類導電高分子的合成與形態研究

學生: 盧曉琪

指 導教 授: 黃華宗

國立交通大學材料科學與工程學系(研究所)博士班

摘 要

本論文研製之聚方酸類高分子(polysquaraine)為包含方酸類(squaraine)有機染料 及π-共軛結構之聚合物,因具有突出的導電性質,而被歸類為共軛或導電性高分子。 本研究中,我們在相同的聚縮合條件下,以方酸(squaric acid)分別反應吡咯(pyrrole) 的衍生物 1-辛基吡咯(1-octylpyrrole)和 3-辛基吡咯(1-octylpyrrole),而製備得導電性 高分子 1-辛基吡咯聚方酸高分子(poly(1-octylpyrrole)squaraine)和 3-辛基吡咯聚方酸 高分子(poly(3-octylpyrrole)squaraine)。合成出的 3-辛基吡咯聚方酸高分子,其分子結 構幾乎都是重覆的兩性離子結構組成;反之,1-辛基吡咯聚方酸高分子,其分子結 構幾乎都是重覆的兩性離子結構組成;反之,1-辛基吡咯聚方酸高分子其分子結構則 是兩性離子結構與共價鍵結構以 2:1 的重覆單位比例組成。我們的研究結果顯示出: 吡咯衍生物與方酸的聚縮合反應,不同位置的烷基對聚方酸類高分子的產物之分子結 構有相當性的影響。

聚方酸類高分子的構造形態,影響其光學、物理和電性特質及應用;所以,控制 聚方酸類高分子的構造形態,對此類材料的研究與應用而言,是一個非常重要的議 題。合成出的導電性高分子 3-辛基吡咯聚方酸高分子,擁有重覆單位的兩性離子結 構;除了可利用不同的陽離子來控制其於溶劑中的構造形態外,我們發現活性金屬也 會引發其構造形態的轉換。經由活性金屬的引發,最可能使這個導電性高分子由線形 結構形態轉換至摺疊態,並且此轉換是可逆的。

Synthesis and Conformation Investigations of Conducting

Polymer Poly(pyrrolyl)squaraines

Student : Hsiao-Chi Lu

Advisor : Wha-Tzong Whang

Department of Materials Science and Engineering College of Engineering National Chiao Tung University

Abstract

Polysquaraines are organic dyes containing squaraines and π -conjugated polymers that have unique intrinsic conductivity and are classified as conjugated polymers or conducting polymers. In this work, poly(1-octylpyrrole)squaraine and poly(3-octylpyrrole)squaraine were synthesized from squaric acid with 1-octylpyrrole and 3-octylpyrrole under identical conditions of condensation. The polysquaraine from 3-octylpyrrole possesses mostly zwitterionic repeating units (>97 %), but the polymer from 1-octylpyrrole consists of zwitterionic and covalent repeating units in a ratio 2:1. This result indicates that the position of the alkyl group in the pyrrole derivative affects the conformation in the condensation of poly(pyrrolyl)squaraine.

The optical, physical and electronic properties of polysquaraines are affected strongly by a variation of its conformation, controlling the conformation is a critical issue for applications based on these materials. Besides induction by metal ions, the conformation of poly(3-octylpyrrole)squaraine as-synthesized having a zwitterionic repeating unit is variable when its solution in trichloromethane makes contact with the surface of an active metal. The conformation of this zwitterionic poly(3-octylpyrrole)squaraine induced by active metals reverted to its original structure on removing contact with the metals. A possible structural alteration of this CP is thus a reversible isomerization from a linear conformer to a folded one induced with an active metal surface.



指導教授

黄華宗教授

國家同步輻射研究中心

鄭炳銘博士

口試委員

黃華宗教授、陳軍華教授、張棋榕教授、許火順博士和鄭炳銘博士在學 生論文口試的指導與建議。

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- 國家同步輻射研究中心

林克剛博士、莊偉綜博士、蔡孟芳小姐、陸秀琴小姐、孟憲英小姐

臺大醫院

黄天祥醫師

曉琪家人

母親與姊姊



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