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摘　　要

於高分子的領域中，其化學性質與物理性質皆具有相當的重要性，且兩者亦是相輔相成。藉由化學改質的方法來滿足某些物理性質的需求、或是以物理性質研究來延續合成產物的應用性與實用性，而本論文主要是以改質高分子的功能性、強化實際使用的可行性、並針對這些新型高分子的物性與化性作一深切的討論。文中以 polybenzoxazine 為研究主體，內容則著重於以下所列之三大主題：

(1) polybenzoxazine 與高分子間作用力以及熱交聯行為之研究

在高分子的物理性質研究中，相容性(Miscibility)和特殊作用力(Specific Interaction)的探討，一直都是相當有趣的主題；且常有助於解釋許多的高分子行為。其中氫鍵作用力(Hydrogen bonding interaction)的探討更是本實驗室多年來研究的主要方向之一，本文研究之主體：polybenzoxazine 可產生氫鍵予體，並可與其它氫鍵受體的高分子產生氫鍵作用力，使得混摻高分子的諸多性質因而大大提昇。再者，藉由對其熱交聯行為深入的研究，將有助吾人控制 polybenzoxazine 各種性質的優與劣，並能徹底瞭解此一新型高分子的各項特性。

(2) polybenzoxazine 於低介電材料之研究

低介電材料一般主要是作為絕緣材料用，它的研究伴隨著積體電路(IC)線寬的縮小日形重要，介電值已由傳統 4 左右的 SiO_2 逐步進展到了 3 以

下，甚至許多的研究已經達到 2 以下的水準，時至今日，介電值小於 3 的材料才真正具有較大的應用性。在不改變現行銅製程的情況下，選用低介電值之材料作為絕緣用，乃是大幅地降低 *RC* delay 影響的最直接方法，這也是為何低介電材料被如此廣泛的研究與討論。而 polybenzoxazine 本身具有一些相當優異的性質，如：交聯後的收縮率趨近於零、熱安定性高、低吸水性、高玻璃轉移溫度…等等，此外，有別於一般高單價的低介電材料，polybenzoxazine 具有相當的成本優勢。吾人以 polybenzoxazine 作為低介電材料的基材，並利用(a)氟化此高分子與(b)製成奈米級的多孔性材料的方法，來降低 polybenzoxazine 的介電值，並開展出 polybenzoxazine 的另一種新用途。

(3) 金剛烷修飾之 polybenzoxazine 與環糊精錯合的基礎研究

本文同時將一個立體阻礙較大的環狀取代基(金剛烷：adamantane)；鍵結到 polybenzoxazine 的高分子鏈上，以提昇此高分子的玻璃轉移溫度。再者，吾人利用金剛烷可和 β-環糊精(β-cyclodrextrin)形成錯合(complex)的特性，使得經金剛烷修飾後的 polybenzoxazine 與 β-環糊精形成具有特殊的晶體結構，並利用廣角 X-ray 散射、^{1}H 液態核磁共振儀與 ^{13}C CP/MAS 固態核磁共振儀來鑑定與探討此一結構與型態，並深入研究此一結構對各種性質所造成之影響。

Abstract

The physical properties and chemical properties are both important in the polymer researches. Many properties will be enhanced after modifying the polymers. In this thesis, we focus on three major subjects which based on the polybenzoxazines:

(1)The studies of polymer interaction and thermal curing behavior of polybenzoxazines

We concentrate on the polymer miscibility and specific interaction, especially in the hydrogen bonding interaction. The polybenzoxazine contains hydroxyl group that is known as a proton donor for several polymers with proton acceptor, and many properties were enhanced after inducing the hydrogen bonding interaction. Furthermore, we could control and understand the properties of polybenzoxazines by studying its thermal cuing behavior.

(2) The studies of polybenzoxazine in low dielectric materials

Low dielectric constant materials ($k < 3.0$) have the advantage of facilitating manufacture of higher performance integrated-circuit (IC) devices with decreasing feature size of the chip. After replacing the aluminum process by the cupper process, the most feasible approach is to use an insulating material possessing a lower dielectric constant without changing the copper process. Polybenzoxazine resins were found to possess several outstanding properties that fit the requirements of low dielectric constant materials, such as near-zero shrinkage after curing, high thermal stability, low water absorption, high glass transition temperature and low price. In the section, we used two methods including fluorinating polybenzoxazine and forming porous structures in the course of developing low dielectric constant materials.

(3) The studies of polyseudorotaxanes based on adamantane-modified polybenzoxazines and cyclodextrin

In general, a polymer containing a cyclic alkyl substitute tends to raise its T_g. In addition, positioning the mass center of the substitute closer to the polymer backbone will increase the bulkiness of the substitute and thus become more effective for T_g increasing. In the section, we incorporated adamantane as a pendant group into the polybenzoxazine structure and enhanced its thermal properties. Furthermore, the pendant group, adamantane, forms stoichiometric complexes with β-cyclodextrin (β-CD) and fine crystalline powders are obtained. We characterized these complexes by powder X-ray diffraction, ^{1}H NMR spectroscopy, ^{13}C and ^{13}C CP/MAS NMR spectroscopies. A detail discussion was made in order to analyze the effect that caused by the crystalline complex structure.