摘要

本論文主要探討高分子薄膜殘留應力與外加電場誘發週期性圖形及塊材輻射處理後退火行為。第一部份製備了聚一氯對二甲苯(Parylene C)薄膜與矽微懸臂樑雙層結構。薄膜呈現連續平整且矽微懸臂樑在鍍膜後略微往上翹曲，此為薄膜與基板間熱膨脹係數不同造成。由其曲率的改變以理論推測鍍膜溫度為 73 ℃。薄膜與基板內的應力分布呈線性且在介面處產生不連續。第二部分為伽瑪輻射照射聚4-甲基-1-戊烯 (PMP)的色心 (color center)產生的色心湮沒(annhilation)動力學機制，其可見光穿透率損失隨輻射累積照射劑量及退火溫度增加而增加，並產生紅位移 (bathochromic)於紫外光/可見光光譜。吸收率數據隨時間變化推測其產生過程為一級 (first order)反應。照射之聚碳酸酯 (PC)內同時存在永久及可經由退火消除的色心，後者可藉由高溫退火而湮沒。色心湮沒機制為一級反應且樣品吸收率與色心濃度成非線性正向相關 (nonlinearly proportional)。第三部分聚甲基丙烯酸甲酯 (PMMA)與聚甲基丙烯酸-2-羥基乙酯共聚物 (PHEMA)產生之自由基於升溫退火下湮沒機制，兩者均推測有三種以上自由基存在。PMMA 與 PHEMA 的 R_a 與 R_b 自由基衰退過程為二級反應，PMMA 之 R_c 自由基為先一級後轉為二級。長時間 PHEMA 的之 R_c 自由基衰退過程為二級反應。兩者同劑量下劑量與退火溫度，自旋濃度隨退火時間增加而下降。最後為電場誘發聚 PC 與 PMMA 薄膜不穩定產生具週期性規律的柱狀圖形。不同薄膜厚度樣品均於實驗初期即產生柱狀結構，薄膜越薄者圖形密度也越低且尺寸較小，且均隨時間增加而上升，趨勢逐漸減緩，於 40 分鐘後圖形穩

定，成長過程與擬合曲線相符。比較不同退火溫度之薄膜穩定圖形，可得出退火溫度較高者，點狀圖形直徑較大且間距較寬。綜合以上兩因素樣品之週期性於同厚度薄膜下，退火溫度越高則週期越長；相同退火溫度下薄膜越厚則週期越長。

Abstract

In the thesis, we studied residual stresses and electric field induced patterns on polymer thin films as well as annealing behavior of polymeric materials after irradiation. In the first part, we built a Parylene C/Si bilayer cantilever structure. The Parylene C thin films were continous and flat on the top of cantilevers. Due to the mismatch of thermal expansion in this system, cantilevers curved and bent towards up. We inferred that the deposition temperature was 73 ^{o}C by observing the curvature variation. Moreover, the residual stress distribution was linear in both layers and discontinued on the interface.

In the second part, we studied the generation kinetics of color centers in gamma ray irradiated poly(4-methyl-1 pentene) (PMP). The transmittance loss in irradiated PMP with increasing gamma ray dose and annealing temperature, and present bathochromic shift in UV/ Vis spectra. The absorptance data were found in good agreement with the first order reaction. On the other hand, the color centers of polycarbonate (PC) will annihilated at elevated temperature after irradiated. The measured absorptance data followed first order mechanism, and the absorptance was nonlinearly proportional to the concentration of annealable color centers. In the third part, we discussed the radicals annihilation of gamma ray irradiated poly(methyl methacrylate) (PMMA) and Poly(2-hydroxyethyl methacrylate) (PHEMA) at elevated temeratures. We inferred that both PMMA and PHEMA had three different radicals at least. The radicals R_a and R_b followed second order process for PMMA and PHEMA. R_c of

PMMA in a short time period followed a first order decay and turned into second order in the long term. R_c of PHEMA followed second order kinetics at longer times. For a given dose and annealing temperature, the concentration of each radical decreased with time. In the last part, we investigated electric field-induced periodical pillar patterns via thin film instability of PC and PMMA. The pillar patterns grew at the initial stage of experiments for both polymers. Thepillars were smaller and less dense for thinner film, and increasing with annealing time. The growth rate was decreased gratually and steadied after forty miniutes. The process of growth were in good agreement with fitted curves. Comparing steadied patterns at different annealing temperatures,diameters and space between pillars were largerat higher annealing temperature. Combining these two factors, we concluded that the periodicity was increasing with increased annealing temperature for the films with the same thickness; the periodicity was increasing with increased film thickness for the same annealing tempaerature.