國　立　交　通　大　學

材料科學與工程學系

博 士 論 文

單軸延伸聚亞醯胺薄膜光學異向性之研究

A Study on Optical Anisotropies Properties of Polyimide Film by a Uniaxial Stretch Method

研究生：金進興

指導教授：黃華宗博士

中華民國九十六年七月

單軸延伸聚亞醯胺薄膜光學異向性之研究

A Study on Optical Anisotropies Properties of Polyimide Film by a Uniaxial Stretch Method

研究生：金進興 **Student：Jinn-Shing King**

指導教授：黃華宗 博士 **Advisor: Dr. Wha-Tzong Whang**

國立交通大學 材料科學與工程學系

A Thesis

Submitted to Department of Materials Science and Engineering College of Engineering National Chiao Tung University In partially Fulfillment of the Requirements for the Degree of Doctor of Engineering In Materials Science and Engineering

July 2007

Hsinchu, Taiwan, Republic of China

中華民國九十六年七月

單軸延伸聚亞醯胺薄膜光學異向性之研究

研究生：金進興　　　　　　　　　　導教授：黃華宗　博士

國立交通大學材料科學與工程學系

摘　　要

本論文主要研究分為二部分：(1)以單軸拉伸方式來探討PI薄膜的光學異向性；(2)探討PI薄膜在拉伸時結構對其雙折射性的影響。首先，我們以動態機械分析儀(DMA)的應力緩和(Stress Relaxation)模式對芳香族FDA-BAPP PI及脂肪族D2192-BAPP PI薄膜進行拉伸實驗,並將拉伸後的PI薄膜置於一組相互交差的偏光片中觀察其光學異向性,發現拉伸後的PI薄膜試片可以降低在±45°視角的漏光的效果，展現出如同A-Plate的光學補償特性，所顯現的光學補償效果相當的均勻而且沒有色偏的情形發生, 證實以拉伸方法可以造成PI薄膜很均勻的雙折射效應。PI薄膜在拉伸時之拉伸力(Pre-load Force)是影響PI雙折射率的重要控制因素，過高的拉伸力(>0.3N)會造成PI薄膜試片的Necking現象，將導致其雙折射率的不均勻。Prism Couping

方法被用來量測PI薄膜的折射率與厚度，藉由雷射光耦合之方式可以在小範圍區域內精確量到PI薄膜的折射率，將經此方式量得的PI薄膜折射率與厚度計算其光學補償值，其結果與直接量測法所得的光學補償值相當，說明以此拉伸方法可以獲得很好的PI薄膜光學異向性。

本論文的第二部分在研究PI分子結構與其雙折性的相互關連性，我們合成7種不同結構之PI並將其薄膜以單軸拉伸之方式作延伸實驗後，量測其In-Plane的雙折射性。在此是以DMA 的另一種試片拉伸方式-Creep模式，來取代之前的Stress Relaxation模式對PI薄膜試片進行拉伸實驗，Creep模式是以最低的拉伸力量及最低的拉伸溫度的前提下，選擇Pre-load Force(N)與Isothermal Temperature(^{o}C)這二項為拉伸控制因素，在此狀態下的PI薄膜拉伸比是取決於其拉伸的時間，此種拉伸模式將可得到較高的拉伸比，而高的拉伸比是獲取較高薄膜雙折射率的必要條件。經拉伸試驗後發現PI薄膜的雙折射率與其分子結構有相當的依存性，其中PI分子的排列程度將影響其拉伸雙折射性的大小。為了釐清PI結構對其拉伸雙折性之影響，我們引用ANDO's團隊所提出的模擬理論，以計算推估出之Dn^{o}為指標來觀察PI結構對其拉伸雙折射性的影響，發現此法與實際量測PI薄膜的雙折射率間，在某一些PI結構上會有預測上的差異，無法準確的預測PI薄膜的拉伸雙折射率。我們考慮到PI薄膜在拉伸時所產生的分子鏈間

交互作用的影響，以其分子鏈排列程度作一修飾參數來對ANDO’s的預估模式作修正, 發現經修正過的預估模式可以較準確的預測PI薄膜結構與拉伸雙折射性之間的關係, 其預測值與實際量測得到的雙折射性呈現較好的一致性，此一致性的結果也經由X-ray繞射實驗結果得到證實。

A Study on Optical Anisotropies Properties of Polyimide Film by a Uniaxial Stretch Method

Student：Jinn-Shing King　Advisor：Dr. Wha-Tzong Whang

Department of Materials Science and Engineering

National Chiao Tung University

ABSTRACT

A new biaxial-retardation film prepared from the uniaxial-stretched polyimide (PI) film was developed for compensating the viewing angle of liquid-crystal displays.

In the first part of this thesis, Stress relaxation method set up in the software of DMA was used to perform the aromatic (FDA-BAPP) and aliphalic (D2192-BAPP) PI film stretching process. To study the optical anisotropies property to the light leakage from the crossed polarizers, we put the stretched samples into one set of crossed polarizers and as expected, the stretched PI films could reduce the light leakage at view angle of ±45 deg, and exhibited a visually observed compensating property of an A-plate. No color shift was

observed, and the birefringence was very uniform. These results prove a uniform birefringence can be obtained by a stretched process for PI films. Preload force is a key factor to control the birefringence in stretched process. The non-uniformity of birefringence induced by necking phenomenon was observed in the sample with high preload force of 0.3.To analyze the birefringence change in stretched PI films, the prism coupling method was used to measure the nx, ny, nz, and thickness of the stretched PI films. The prism coupler method can sense local deviation of birefringence better than direct retardation measurement. It may be due to the smaller beam size of Hi-Ni laser used in prism coupling. In conclusion, the biaxial retardation of uniaxial-stretched PI films was confirmed by both methods of RI measurement and direct retardation measurement and obtained a good optical anisotropies property.

The second part of this thesis is to study the relationship between PI film structural and birefringence property. Seven polyimides (PI) were synthesized and their films were uniaxially stretched to observe the variation in their in-plane birefringence. The creep method of DMA was used instead in stretching the PI films. The preload force (N) and isothermal temperature (^{o}C) were the two controlled factors that were chosen on the basis of the lowest stretchable force and lowest temperature for each PI structure. The elongation ratio of a PI film was then decided by the stretching time. Creep method can be reduce the necking phenomenon was observed and obtained high elongation ratio in the stretched process for PI film specimens. After the stretched process, the birefringence of PI

have a strong relationship with it's molecular structural. To clarify the structural effect on the stretch-induced Δn in PI films, we followed ANDO's method to estimate the Δn^{o} of each PI structure. We found the birefringence from ANDO's estimate method has some different comparing with measured by prism coupler. For modified the ANDO's model, we used a molecular orientation degree factor in PI film stretched process to revise this model. We can obtain an accurate estimated stretched birefringence of PI film after revised model. Prism coupler measured also has same results proved by X-ray diffraction testing.

目錄

中文摘要 IX

英文摘要 IX

目錄 IX

表目錄 IX

圖目錄 IX

一、緒論 1

1-1 聚亞醯胺材料介紹 1

1-2 聚亞醯胺的合成 3

1-3 聚亞醯胺的結構與光學異向性 7

1-4 液晶顯示器的視角補償 12

1-5 位相差膜的補償原理與種類 15

1-6 位相差膜的製造 20

二、文獻回顧與研究動機 24

2-1 文獻回顧 24

2-2 研究動機及目的 39

三、實驗部分 37

3-1 單體試藥 37

3-2 溶劑及其它材料 38

3-3 儀器設備 39

3-4 試藥的前處理 40

3-5 聚醯胺酸(PAA)的合成 40

3-6 聚亞醯胺(PI)膜的製作 41

3-7 聚醯胺酸(PAA)的黏度分子量量測 42

3-8 玻璃轉移溫度(Tg)量測 43

3-9 穿透率(Transparency)量測 44

3-10 霧度(Haze)的量測 44

3-11 以動態機械分析儀(DMA)進行PI薄膜的拉伸 46

3-12 折射率之量測 48

3-13 X-ray 繞射測試 50

3-14 偏極化紅外線光譜(Polarized FT-IR)量測 51

四、結果與討論 53

4-1 拉伸對聚亞醯胺薄膜雙折射性之探討 53

4-1-1 PAA 合成與 PI 製膜 53

4-1-2 PI薄膜的拉伸 54

4-1-3 PI 光學異向性的探討 55

4-1-4 PI結構與其光學異向性的關聯 63

4-2 聚亞醯胺結構對其拉伸雙折射性之影響 65
4-2-1 PI合成與其特性測試 65
4-2-2 DMA Creep 69
4-2-3 PI結構對其光學異向性之探討 70
4-2-4 PI 雙折射性預測之模式建立 74
4-2-5 PI分子鏈的排列性 80
五、結論 86
六、參考文獻 90
七、期刊著作 96

表目錄

表1-1 位相差膜的品質特性要求 20

表4-1 七種不同結構PI薄膜特性表 69

表4-2 七種不同結構PI薄膜模擬估計值與量測特性 76

表4-3 PI薄膜的分子鏈排列預測方程模式 81

圖目錄

圖 1-1 PI 應用於 IC 構裝之示意圖 2

圖1-2 泛用高分子材料的長期耐溫比較 3

圖 1-3 PI 合成反應方程示意 5

圖 1-4 二酐與二胺反應形成 PAA 的反應動力方程 6

圖 1-5 光折射過程的示意圖 9

圖 1-6 Prism Coupler 法量測高分子薄膜折射率的示意 10

圖1-7 相差模作LCD視角補償之示意 15

圖1-8 以VA 模式為例說明位相差膜的補償原理 16

圖1-9 WV film的補償原理 17

圖 1-10 大尺寸 VA 面板的補償原理 19

圖 1-11 位相差膜的延伸方法 22

圖1-12 高分子延伸膜的折射率控制 22

圖2-1 液晶顯示器的視角問題與光學補償膜之功能 25

圖2-2 可為C-Plate光學補償之具有多苯環剛硬結構的PI分子 27

圖2-3 以PI為C-Plate材料做LCD光學補償之示意 28

圖 2-4 旋轉結構之光學補償膜的結構原理 29

圖2-5 以碟狀液晶方式作光學補償膜之示意 31

圖2-6 以雙軸延伸方式達成雙光軸補償之示意 32

圖 3-1 三通 Ubbelohde 毛細管黏度計 43

圖3-2熱機械分析儀(TMA) 44

圖 3-3 紫外線光譜分析儀量測薄膜 Haze 之示意說明 46

圖3-4紫外線光譜分析儀搭配積分球 46

圖 3-5 用來高溫拉伸 PI 薄膜的 TA DMA 2980 48

圖 3-6 SPA-4000 量測光波導材料傳輸損失之原理示意 49

圖 3-7 SPA-4000 折射率量測儀 50

圖3-8偏極化紅外線光譜的測試原理示意 51

圖4-1 D-B及6F-B單體之PI結構 53

圖4-2 DMA夾具圖示 55

圖4-3 拉伸PI薄膜不同視角之漏光比較示意 56

圖 4-4 Refractive indexes of each axis, nx, ny and nz, in D-B films (a) and in 6F-Bfilms (b) at different elongation ratios. 59

圖 4-5 The birefringence of stretched D-B films at different preload Force 60

圖4-6 The retardations, R0 (a) and Rth (b), of the stretched D-B films which were evaluated by a prism coupling method and a direct retardation measurement. 62

圖4-7 6FDA, D2192, PMDA, ODPA, ODA, DDM, DMDDM, and BAPP used for synthesizing PIs in stretch-induced birefringence studies. 66

圖4-8 7種PI薄膜UV穿透光譜 68

圖 4-9 Variations in in-plane birefringences (Dn) induced by both stretching methods of stress relaxation (S&R) and creep, compared with two polyimide films of D2192-BAPP (a) and 6FDA-BAPP (b) structures. The Dn data of each polyimide were fit to the curve of a binomial. 71

圖 4-10 Variations in in-plane birefringences induced from elongation change of PI films that were prepared from seven different PIs of D2192-BAPP, D2192-ODA, D2192-DDM, D2192-DMDDM, PMDA-BAPP, ODPA-BAPP, and 6FDA-BAPP. 73

圖 4-11 7 種不同結構 PI 薄膜的 TMA 量測圖 77

圖4-12 Wide-angle X-ray diffractograms of stretched PI films of PMDA-BAPP (a) and ODPA-BAPP (b). The elongation of two PI films is 130% 79