

Chemically Induced High Pretilt Angle by CN-Containing Polyimide

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Abstract

New copolyimides containing nitrile side group were synthesized from copolymerization of pyromellitic dianhydride, *m*-phenylene diamine and 3,5-diaminobenzonitrile and subsequent thermal imidization of the resulting poly(amic acid). Crystallinity, glass transition temperature and initial decomposition temperature of copolyimides were almost identical to those of homo polyimide prepared from PMDA and *m*-PDA. Change of pretilt angle induced by the orientation layer of resulting copolyimide was investigated by using a nitrile-containing nematic liquid crystal cell after rubbing. As the content of polar nitrile group was increased in the copolymer, pretilt angle was increased from 3.65° to 6.49°. The mechanism of this was speculated as the dipolar interaction between the liquid crystal and nitrile groups in copolyimide.

Introduction

Homogeneous alignment of liquid crystal on the orientation layer are important fundamentally as well as technically [1]. In numerous polymeric orientation layers, the rubbed polyimides are the most commonly employed material due to its excellent thermal property, chemical resistance, low dielectric property and stable aligning characteristic.

The pretilt angle Θ_p , which is defined as the angle made by liquid crystal (LC) molecules and the rubbed surface, affects the electro-optical characteristics of LCD devices, such as image quality, viewing angle and contrast. Thus the development of orientation materials with high Θ_p is essential to prepare a high quality LCD devices. There are numerous reports concerning the mechanism of LC alignment based on the geometrical, physical and chemical theories. Among them, the importance of microstructural environment between LC molecules and orientation surface is received much attention recently to understand the aligning in the molecular level. Toney et al. reported that the aligning of molecules is achieved in the range of near-surface area [2]. Murata et al. reported that the polymer chains or side chains on the surface of orientation layer affect the LC alignment [3]. The steric and electronic interactions between LC molecules and orientation polymer induced by chemical and physical nature of its side chain are also important as reported by Lee et al. [4]. They also reported [5] the non-polar side chain of polyimide orientation layer provided relatively large pretilt angle while polar side chain gave small pretilt angle due to the microscopic molecular reorientation of a polymer surface induced by rubbing, i.e., the stronger electronic interaction gave the smaller Θ_p , and the greater steric repulsion results in the larger Θ_p .

In this presentation, wholly aromatic copolyimides containing nitrile moiety that is also present in the LC were synthesized and their molecular interaction with LC molecules was investigated by measuring the pretilt angle induced by the copolyimides.

Experimentals

Pyromellitic dianhydride (PMDA) and *m*-phenylene diamine (*m*-PDA) were purified by sublimation at reduced pressure. 1-Methyl-2-pyrrolidinone (NMP) was used after drying with calcium hydride and a subsequent vacuum fractional distillation. Nematic LC for the Θ_p measurement was E7 purchased from E. Merck (a mixture of four different CN-substituted alkyl phenyl compounds

with different alkyl length and number of phenyl rings). 3,5-diaminobenzonitrile (3,5-DABN) was synthesized via Pd/C catalyzed reduction of 3,5-dinitrobenzonitrile in 90 % yield. Copolymerization was carried out by using a conventional method of poly(amic acid). After dissolving *m*-PDA in NMP completely, PMDA and 3,5-DABN was added with 1 h interval and the reaction mixture was stirred for 24 h at room temperature under nitrogen atmosphere. The resulting solution was spin-coated on a ITO (10 X 10 mm) or glass substrate and placed under reduced pressure at 80 °C for 2 h. The poly(amic acid) film was heated to perform a thermal imidization at 150, 200, 250 and 300 °C for 30 min respectively and 350 °C for 1 h under nitrogen atmosphere. The content of 3,5-DABN with respect to the total moles of dianhydride was controlled to be 0, 5, 10, 15, 25, 50 and 100 % and the names of those samples were abbreviated as PMD-0, PMD-5, PMD-10, PMD-15, PMD-25, PMD-50 and PMD-100, respectively. The structure and physical properties of the copolyimides were characterized by Fourier-transform infrared spectroscopy (FT-IR), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) and X-ray diffraction (XRD). Polyimide films used for pretilt angle measurements were 100 ± 5 nm in thickness as determined by a Alpha Step 200 surface profiler (Tenco Instruments) and rubbed with a velvet cloth by using FSA90-011M rubbing machine (Wande Co.). The rubbing condition was set at roller speed (*n*) of 1380 rpm, speed of stage (*v*) 7 cm/sec, pile impression of 0.5 mm, roller diameter of 5 cm, and number of rubbing of one. Cell gap was controlled to be 30 μm and the cell was assembled with two anti-parallel substrates followed by injection of E7, at isotropic temperature (100 °C). The Θ_p was measured by using crystal rotation method as described in other literature [6]. Three different point of a cell was measured and the values were averaged to define a Θ_p .

Results and Discussions

The synthetic scheme of copolyimides containing nitrile groups is shown in Scheme 1. The thermal imidization of poly(amic acid) precursor was monitored by comparing FT-IR spectra of PMD-100 during the thermal treatment at different temperature those of other PMD series. It was found that as the content of nitrile moiety, peak corresponding to CN triple bond vibration was increased at 2236 cm⁻¹ and their peak intensity ratio compared to those at 1780 cm⁻¹

(imide carbonyl) exhibited a linear relationship with respect to the mole fraction of 3,5-DABN in the copolymer (Figure 1). Comparison of XRD patterns of PMD-0, PMD-50 and PMD-100 also revealed that there is no appreciable difference in crystallinity.

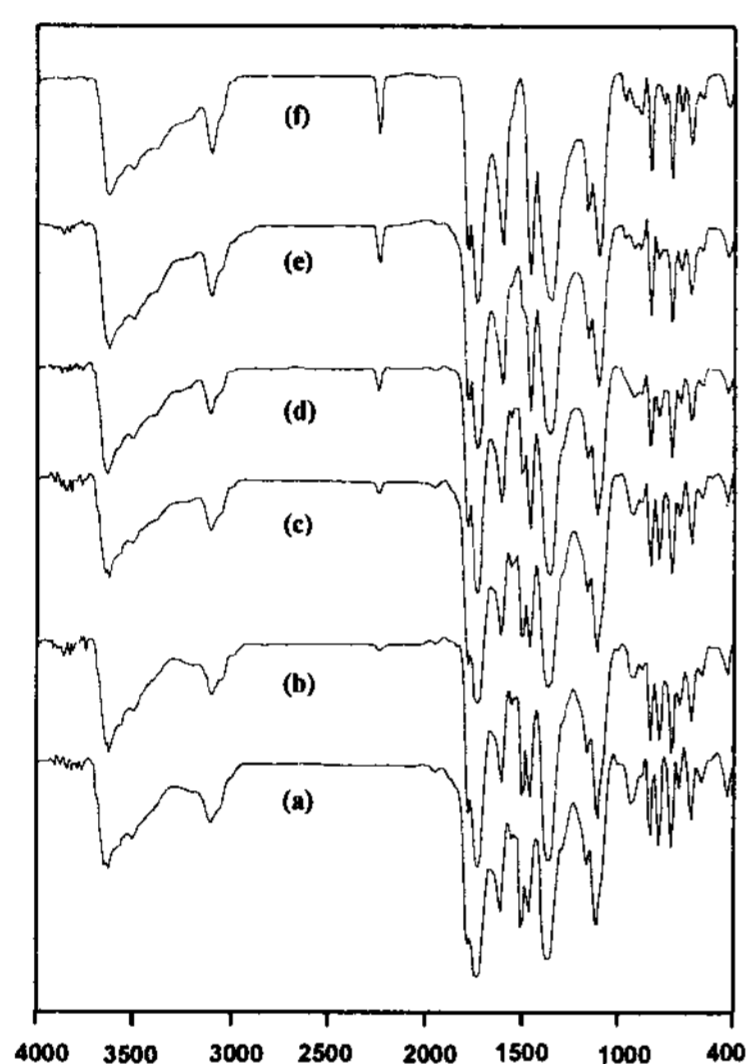
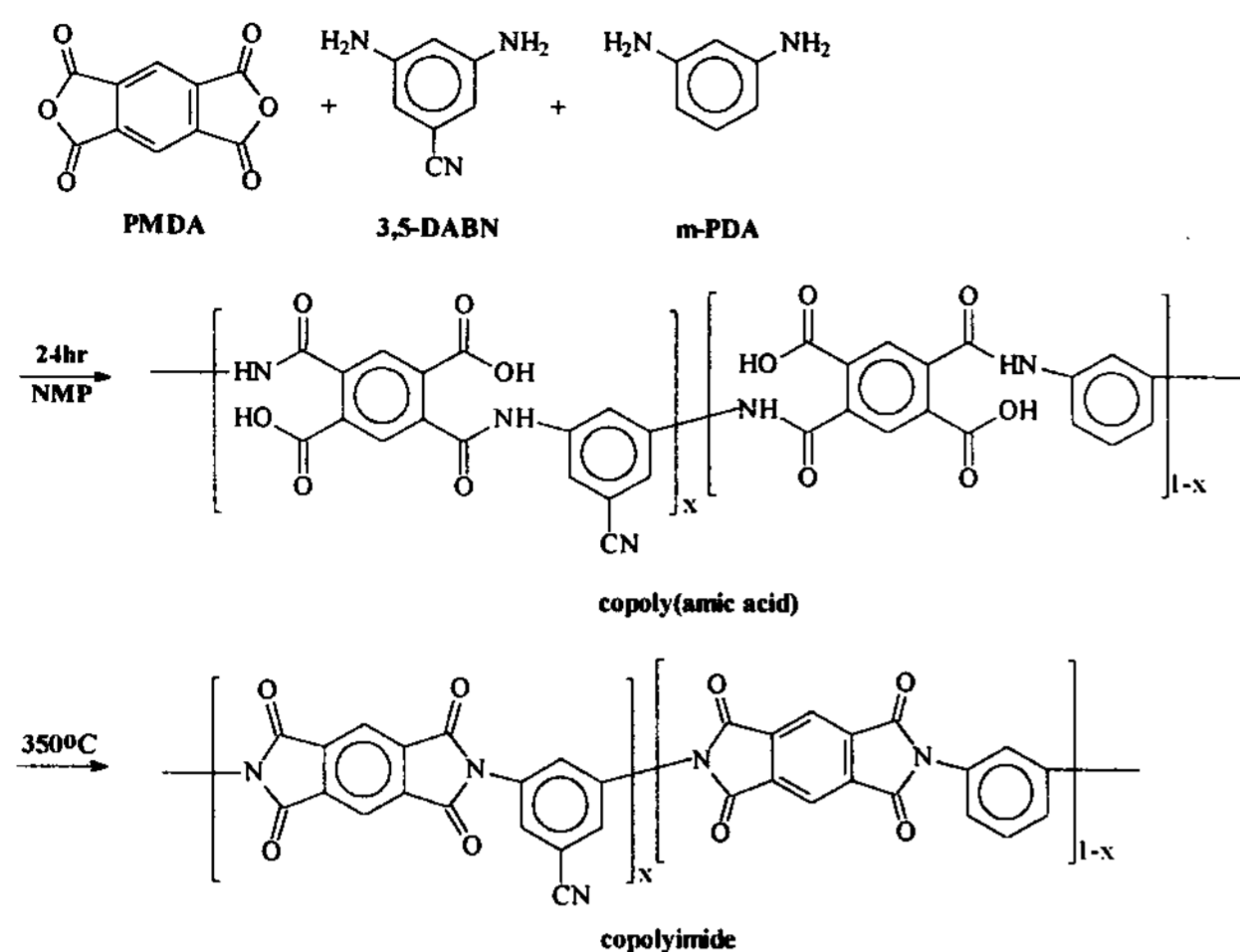


Figure 1. FT-IR spectra of PMD series: (a) PMD-0, (b) PMD-10, (c) PMD-20, (d) PMD-50, (e) PMD-75, and (f) PMD-100

Table 1 summarized the results of thermal analyses. Glass transition temperature (T_g) was found to be 340 ~ 364 °C. However, we were not able to find any relationship between T_g and the nitrile content of polymer. The wide distribution of T_g values was probably due to the experimental errors, not depending on the chemical structure of copolyimides. Thermal decomposition temperatures (T_{di} for initial and T_{d5} for 5% decomposition) also showed no appreciable difference depending on the content of nitrile moiety. All the polymers were thermally stable up to 440 °C with a similar char yield (ca. 60 %).

Table 1. Thermal analyses results of copolyimide.

PMD	0	10	20	50	75	100
T_g	352	340	347	360	345	364
T_{di}	449	461	450	445	452	449
T_{d5}	517	531	520	501	520	513

All these results indicated that the incorporation of nitrile moiety in the polyimide backbone induced no considerable changes in the physical nature of copolyimide in terms of T_g or crystallinity. However, the pretilt angle measurements of the cell using nematic CN-containing liquid crystal mixture showed that there is a remarkable dependence on the 3,5-DABN content (Figure 2). As the content of 3,5-DABN was increased up to 25 %, the Θ_p was increased almost linearly, and then saturated to a certain value.

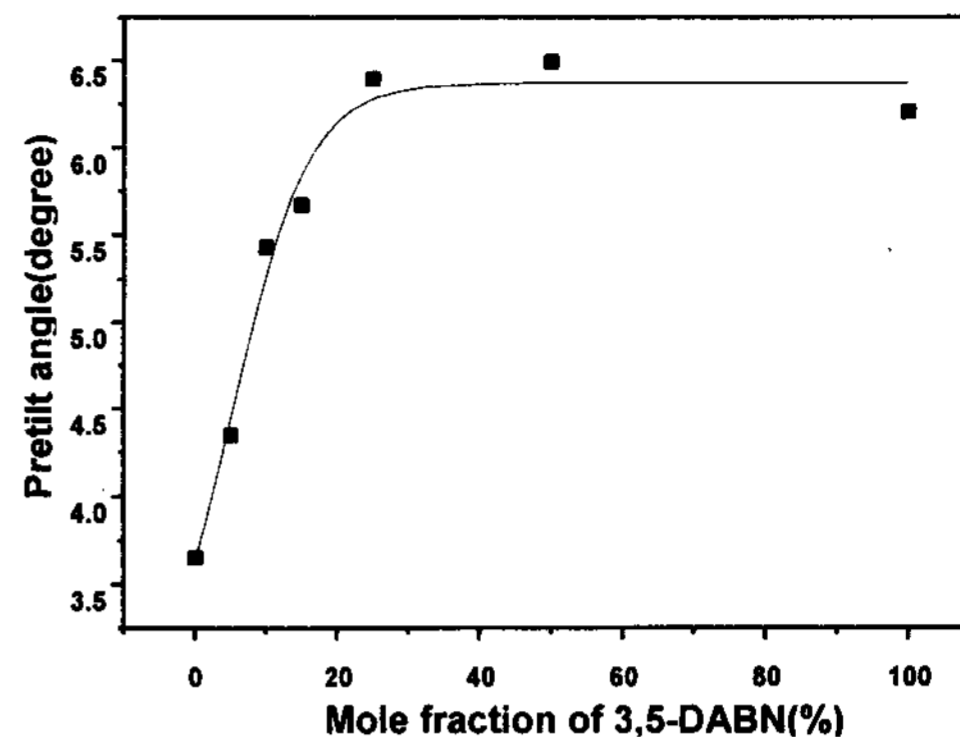


Fig. 2. Pretilt angle change for copolyimides of various mole fraction of 3,5-DABN

These results indicate that polar side groups of polyimide orientation layer could interact electronically with liquid crystal molecules so as to provide high pretilt angle, which is contradictory to generally believed idea that the non-polar side chain of polyimide orientation layer only can provide large pretilt angle while polar side chain gives small pretilt angle [4,5]. The increased pretilt angle by polar interaction is probably attributed to the molecular interaction of benzonitrile groups of copolyimide with those of LC molecules. Similar interactions can also be found in the dimer coupling of LC molecules as reported by Allman et al. [7]. Since the high tilt induced by polar groups has never been reported, we are investigating this phenomenon by using other nitrile-containing polyimides. Further results will be published in the near future.

Conclusion

A series of copolyimides containing nitrile group was synthesized and their effects on the pretilt angle of anti-parallel LC cell were investigated. Unlike previous theories, the more polar side chain of orientation layer provided the larger pretilt angle.

References

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