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The influence of fluorine atoms introduced into the surface of polyimide films by direct fluorination on the liquid crystal alignment

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Fluorinated bulk polyimide (PI) films are usually preferred as alignment layers in liquid crystal displays. We performed a novel approach to obtain surface-fluorinated PI films by fluorine/nitrogen (F_2/N_2) direct fluorination. The results of attenuation total reflection Fourier Infrared Spectrum test (ATR-FTIR) and X-Ray photoelectron spectroscopy indicate that fluorine atoms were introduced into the surface of PI films, and the surface energy of the PI films increased from 47.50 to 69.86 mN m^{-1}. At the same time, the volume of the F atom is larger than that of the H atom, which results in in-situ enhancement of the rigidity of the side chains and alkyl spacers relative to the surface of the PI film, which has taken more upstanding conformation after fluorination. Unexpectedly, the pretilt angle of the PI alignment films can be enormously improved by fluorination by more than 20°, and the magnitude of pretilt angle depends on the content of fluorine atoms introduced.

Keywords: polyimide alignment film; direct fluorination; pretilt angle

1. Introduction

Alignment layers are extensively used in the production of liquid crystal displays (LCDs) in order to orient the liquid crystal (LC) molecule to give a desired optical effect. In the mass production of LCDs, polyimide (PI) alignment layers play a critical role because of their excellent properties with respect to chemical resistance, thermal stability, adhesion to substrates, high resistivity and transparency in the visible spectrum [1]. Typical main-chain PIs (for example, pyromellitic dianhydride octadecylamine (PMDA-ODA)) possess the ability of aligning LC molecules by rubbing, while they can only generate pretilt angles no larger than 3° [2]. For super twisted nematic (STN) LCDs and thin film transistor (TFT) LCDs, pretilt angles ranging from 5° to 20° are needed; in particular, for multi-domain vertical alignment (MVA) LCDs, the pretilt angle of 90° is a must. To raise the pretilt angle, one of the most significant scientific ideas is to introduce side chains on PI backbones. Usually the side chains are end-capped by long alkyl groups or fluorinated alkyl groups. For example, Lee *et al.* [3] synthesised PIs with two (*n*-alkyloxyl)biphenyloxy) side chains, which had good aligning ability. Kim *et al.* [4] prepared a series of PIs with 6-(4-biphenylmethoxy)hexyloxy groups or 6-(biphenoxy)hexyloxy isomers and the pretilt angles were no higher than 27°. However, the instability of the long alkyl groups means that the pretilt angle cannot be kept constant during use [5]. In order to further improve the stability of the pretilt angle, alicyclic or fluorinated alkyl groups have been introduced into the PI system, but introducing fluorinated alkyl groups is more effective and practicable. For example, Nishikawa [6] synthesised PIs with (trifluoromethyl)phenyl groups, which induced the pretilt angle up to 40°. Liu *et al.* [7] synthesised fluorinated PI alignment films that possess pretilt angles greater than 20°. At the same time, the fluorinated PI alignment films are used principally in industry. However, the synthesis of diamines or dianhydride-containing fluorinated alkyl groups is difficult and costly, and PI alignment films using the given chemical structures of fluorinated diamine or fluorinated dianhydride do not satisfy the simultaneous different needs of pretilt angles for STN LCDs, TFT LCDs and MVA LCDs.

Therefore, in this paper we performed a novel approach in order to obtain only the surface fluorinated PI alignment films by fluorine/nitrogen (F_2/N_2) direct fluorination. The technique of direct fluorination has been used to prepare polyethylene fuel tanks for the improvement of barriers to fuel oils [8]. Our primary results of fluorinated PI alignment films by F_2/N_2 direct fluorination showed that fluorine atoms were introduced into the surface of PI films and changed the chemical structure and properties of the surface. A series of fluorinated PI alignment films with different pretilt angles can be obtained using the same kind of PI film, and the pretilt angle can be higher than 20°, which depends on the content of the fluorine atoms introduced. This result may provide a new way to adjust pretilt angles of LCs discretionarily on only one alignment layer matrix according to the requirement of different kinds of LCDs.

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2. Experimental

2.1 Materials

Solvent: *m*-Cresol was obtained from the TinXing Chemical Company.

Reagents: 4, 4′-oxydianiline (ODA) was obtained from the ChangShou Chemical Company, and was recrystallised in ethanol. 4, 4′-oxydiphthalicanhydride (ODPA) was obtained from the Shanghai Synthetic Polymer Research Institute and used after further recrystallisation in acetic anhydride. 6-(4-phenyl phenoxy) hexyl-3,5-diaminobenzoate (DABBE6) was synthesised by ourselves. The synthetic route was performed in analogy to a general scheme outlined by Liu *et al.* [9]. The F_2/N_2 (25 vol%) mixed gas was obtained from China Nuclear Honghua Specialty Gases Co., Ltd, and used as received; the amount of impurities (oxygen and hydrogen fluoride) was less than 0.2 vol% in the mixed gas.

2.2 Synthesis of polyimide dope

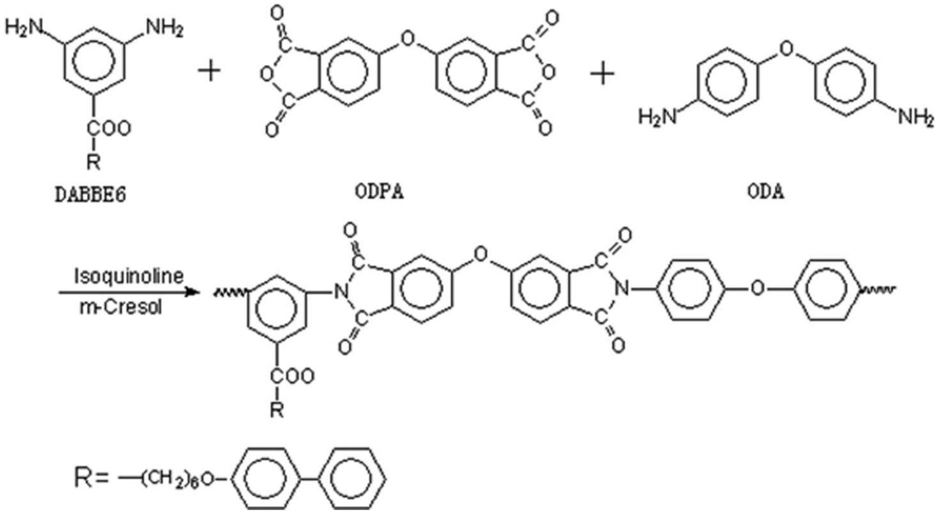
1.5013 g (0.00372 mol) of DABBE6 and 1.1160 g (0.00585 mol) of ODA were dissolved in 30 ml of *m*-cresol in a four-necked 100 ml flask equipped with a stirrer, a nitrogen inlet and an outlet tube. After the mixture had been stirred at 30°C for 30 min, 2.8800 g (0.0093 mol) of ODPA and isoquinoline (1.0 ml) were added, and the temperature of the reaction mixture was raised from room temperature to 170–180°C in 30 min. The reaction was kept at 180°C for 3–5 h with continuous stirring under the flow of dry nitrogen. The PI dope was an isotropic solution with an inherent viscosity of 0.67 dL g^{-1}. The polymerisation procedure is shown in Scheme 1.

2.3 The preparation of fluorinated PI alignment films

PI solutions were spin coated on 25 × 25 mm^2 calcium fluoride (CaF_2) plates at 500 rpm for 5 s and 1500 rpm for 10 s, respectively, followed by curing at 100 and 200°C each for one hour to give touch films. Then, fluorination was carried out in a closed stainless steel (SUS316) reactor equipped with vacuum line. The reaction was run for 1 to 120 min at room temperature with 0.01–1.0 atm fluorine gas. After fluorination, the remains of the F_2/N_2 gas were removed by vacuum to be absorbed in an alkali aqueous solution. Then the fluorinated PI films spin-coated on CaF_2 plates were taken out and preserved in dry atmosphere.

2.4 LC cell fabrication and pretilt angle measurement

The prepared fluorinated PI films on the CaF_2 plates were subsequently rubbed with a roller-covered commercial rubbing cloth, and the rubbing strength L was calculated as follows: $L = lN(2\,\pi rn/60\,\upsilon - 1)$, where L (mm) is the total length of the rubbing cloth that touches a certain point of the film, l (0.3 mm) is the contact length of the rubbing roller circumference, N is the cumulative number of rubbings, υ (17.2 mm s^{-1}) is the velocity of the substrate stage, and n (700 rpm) and r (22.5 mm) are the rubbing roller speed and radius, respectively. LC cells were fabricated from two pieces of rubbed, fluorinated PI films on the CaF_2 plates assembled in an antiparallel rubbing direction with 43 µm (cell gap) thick spacers and filled with 4-pentyl-4′-cyanobiphenyl (5CB) by the capillary method.



Scheme 1. Polymerisation of copolyimides containing biphenyl mesogenic side-groups with six methylene spacers.

3. Characterisation

The Fourier Infrared Spectrum test (FTIR) was carried out on Nicolet 560 FTIR equipment. A ZnSe pellet was used as the reflection plate in the attenuation total reflection FTIR (ATR-FTIR), and the incident angle was 45°. The surface energies of the PI film were tested on drop sharp analysis (DSA) 100 Krüse auto visual contact angle test equipment. The X-ray photoelectron spectrum (XPS) was obtained from XSAM800 XPS equipment. The pretilt angles for the fabricated LC cells were measured by a crystal rotation method with a PAT-20 measurement device (Chanchun Liancheng Instrument Co., Ltd.). The inherent viscosity was determined using an Ubbelhode viscometer and the PI solution containing 0.5% solid (w/w) in *m*-cresol at 30°C. The computer simulations were performed using the Materials Studio 4.0 software from Accelrys Inc.

4. Results and discussion

4.1 Surface energies

The surface of the PI film is the research core of alignment layers, since it straightforwardly contacts and aligns LC molecules and generates pretilt angles. The surface energies can provide some information about the surface. The surface energies of the modified PI films under different fluorine partial pressure (P) and fluorinated time (T) are shown in Table 1; the fluorination reaction temperature was fixed at room temperature (about 25°C).

From the results of the surface energies in Table 1, it can be seen that as the fluorination intensity increases (as a result of the fluorine partial pressure (P) or time (T) of fluorination increasing), the total surface energies increase and are higher than those of the untreated PI films. However, the dispersive component of the total surface energy was considerably lowered, and the polar component increased to 20–30 mN m^{-1} during fluorination, which indicates that direct fluorination can increase the surface energy of PI film, which results from the polarity increasing.

Table 1. Influence of different fluorination processes on surface energy.

Fluorination process	The polar component, mN m^{-1}	The dispersive component, mN m^{-1}	Total surface energies, mN m^{-1}
The virgin PI films	4.45	43.04	47.49
$P = 50$ kPa, $T = 0.5$ h	24.29	26.73	51.02
$P = 100$ kPa, $T = 1.5$ h	30.02	27.12	57.14
$P = 400$ kPa, $T = 18$ h	37.13	25.85	62.98

4.2 Surface structure of PI films after fluorination

In order to further investigate the surface modification, the change of the surface chemical structures of the fluorinated PI film before and after fluorination was investigated by ATR-FTIR measurements as shown in Figure 1.

Figure 1 shows that the absorption strength at 2849–2958 cm^{-1} ascribed to the C–H of the alkyl groups in side chains of PI films decreased obviously with the increase of fluorination intensity. One more peak at 1000–1400 cm^{-1} for the C–F bond was observed on the surface of the PI films after fluorination. These results indicate that some alkyl spacers in the side chain were turned to C–F bonds during fluorination, while the PI units at the surface of the material were replaced by a more complex structure.

To elucidate quantitatively the surface composition after fluorination, XPS experiments were employed. Figure 2 shows the XPS survey scan spectra of the PI film, Figure 2(b) shows the Carbon 1s (C1s) spectrum, and Figure 2(a) shows the Fluorine 1s (F1s) spectrum. From the results of the XPS experiments, different carbon–fluorine covalent bonds, as different binding energy of C–F and C–F$_2$, etc, were introduced into the surface of the PI film after fluorination. The F1s/C1s ratios of the fluorinated PI films under different fluorination conditions ($P = 48$ kPa, $T = 0.5$ h; $P = 100$ kPa, $T = 0.5$ h; $P = 100$ kPa $T = 1.5$ h; $P = 100$ kPa, $T = 4$ h) were 0.16, 0.28, 0.41 and 0.74,

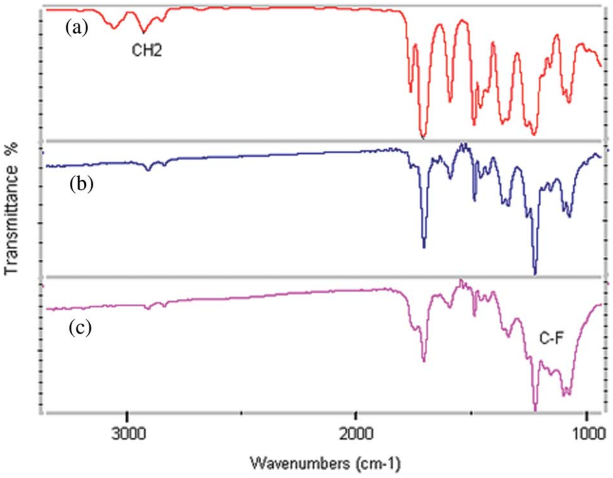


Figure 1. ATR-FTIR of the PI films under different fluorination conditions. ((a) virgin films; (b) fluorinated films under $P = 100$ kPa, $T = 0.5$ h; (c) fluorinated films under $P = 100$ kPa, $T = 1.5$ h).

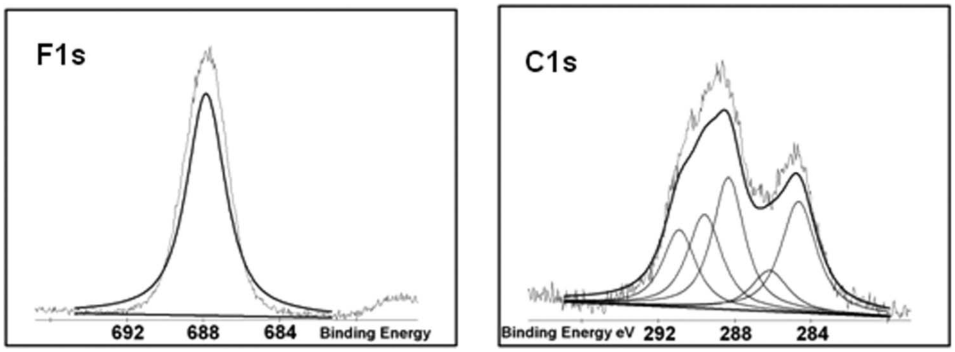


Figure 2. The XPS results of the fluorinated PI films ($P = 100$ kPa, $T = 1.5$ h).

respectively, which increase with increasing fluorination intensity. This can be attributed to the increase of carbon–fluorine functional groups on the PI surface with fluorination. The results of the XPS experiments also agree with the results of the ATR-FTIR, which may explain why the total surface energy rises with increasing fluorination intensity by the increase of carbon–fluorine polar groups.

4.3 *Liquid crystal-aligning property*

Pretilt angles were measured by the crystal rotation method. In our group, a series of PIs containing (biphenyloxy)-n-alkyl groups have been synthesised [10–12], but no large pretilt angle was obtained with these PIs (generally the pretilt angles were about 5–10°). However, pretilt angles of 6.4° and 11.4° were obtained when the F1s/C1s ratios of the PI films were about 0.0 and 0.16, respectively. As for the higher F1s/C1s ratios, such as 0.41 and 0.74, the pretilt angles could not be measured because they lie in the 'dark zone' [4], which arose from the limitation of the crystal rotation method. In this case, the pretilt angles should be between 20° and 70°, which indicates that the pretilt angles of PI films containing side chains with alkyl spacers were improved considerably after fluorination. From this result, it could be seen that the pretilt angle largely depends on the content of fluorine on the surface of the PI film. Combining the foregoing results of the surface energy, the greater the content of fluorine atoms on the surface, then the higher surface energy and the larger the pretilt angles will be. Generally, as the surface energy of PI alignment films decreases, the pretilt angles increase [13], which is in conflict with our results. In order to explore preliminarily the reason for this conflict, computer simulation was employed and the result is shown in Figure 3.

Due to the larger volume of fluorine atoms compared with hydrogen, the rigidity of the side chains would be in-situ enhanced, and the alkyl spacers relative to surface of the PI film would more likely take upstanding conformation after fluorination. At the same time, the C–H binding energies on the PI macromolecules with different chemical surroundings were calculated by computer simulation. The binding energy of C–H in alkyl spacers was the lowest in all C–H of the PI macromolecules. The calculation results indicated that the C–H of alkyl spacers is preferred to be displaced by C–F during fluorination. Therefore, we suggest that side chains with upstanding conformation after fluorination may more easily interact with 4-pentyl-4-*n*-cyanobiphenyl, which induced the 5CB to take upstanding conformation and thus show a higher pretilt angle. However, whether this kind of upstanding conformation is stable under thermal stress,

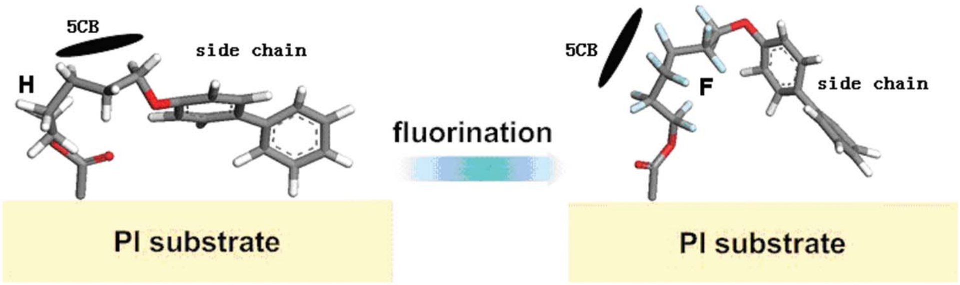


Figure 3. Computer simulation results of PI films after fluorination.

the alignment LC cells using fluorinated films as the alignment layer were baked in oven at 50, 100 or 120°C for 2, 5 or 10 hours, respectively. The pretilt angles of the fluorinated PI films are also more than 20° at all times, which indicates that upstanding conformation of the fluorinated side chains after thermal treatment maintains obviously. More detailed researches are being carried out.

5. Conclusion

Surface fluorinated PI alignment films were obtained by a novel approach of fluorine/nitrogen (F_2/N_2) direct fluorination. The results of the ATR-FTIR and XPS experiments indicate that fluorine atoms were introduced into the surface of the PI films, which resulted in the increase of surface free energy, and the pretilt angles can be improved enormously to greater than 20°, depending on the content of the fluorine atoms introduced.

Acknowledgments

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