

Syntheses and Characteristics of Polyimides for the Applications to Alignment Film for Liquid Crystal Display

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ABSTRACT: In this work, several polyimides (PIs) containing diphenyl ether group were synthesized and characterized by Fourier transform infrared spectroscopy and thermogravimetric analysis. The relationship between the surface structures and the molecular chain conformations of the PIs, whether helical or zigzag, was discussed. The effects of the molecular chain conformations of the PIs on the pretilt angles of liquid crystal molecules were systematically investigated. The surface orientations of polyimides whose chains adopt zigzag and planar conformations were less improved by rubbing treatment than those of polyimides whose chains adopt helical and nonplanar conformations, because the polyimide chains of zigzag and planar conformation are easily packed. The polyimides, whose chains adopt helical and nonpolar conformations, gave larger pretilt angles than the polyimides whose chains adopt zigzag and planar conformations. The pretilt angles measured under the condition of rubbing depth of 0.5 mm were smaller than under the condition of rubbing depth of 0.3 mm. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 2365–2371, 2001

Key words: polyimides; chain conformation; liquid crystal display; pretilt angle; rubbing

INTRODUCTION

Polyimides (PIs) have been widely used as an insulating material for microelectronic devices because of their excellent properties of thermal and chemical stability and low dielectric constant.^{1–3} However, the aromatic PIs are usually intractable because of their insolubility to common organic solvents. Therefore, the most widespread route for the preparation of aromatic PIs is the two-stage polyaddition and polycondensation of a diamine in an aprotic solvent, such as *N,N*-dimethylacetamide and *N*-methyl-2-pyrrolidinone.

A soluble poly(amic acid) (PAA) is obtained as the imide prepolymer in the first stage, and then cyclodehydration of this intermediate polymer, either by heat or by chemical reagents, yields a PI.⁴

On the other hand, liquid crystal displays (LCDs) have become commonplace in all aspects of our information stage.⁵ Polarized light is transmitted and rotated by the liquid crystal (LC) molecules. For the condition of crossed polarizer, light is transmitted through the second polarizer. If an electric field is applied to transparent conductors, molecules rotate and light transmits through a cell without rotation. The second polarizer absorbs the incoming light and the cell appears dark. If the second polarizer is aligned parallel to the first, then light is transmitted with the applied field. To use a LC as a device element,

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uniform alignment of the LC is required. There are several methods to align an LC at the surface, including rubbing,⁶ oblique evaporation,⁷ photoanisotropic alignment,⁸ Langmuir–Blodgett film,⁹ and stamped-morphology¹⁰ processing. Of these methods, polymer alignment layer rubbing is generally used because of its capability for mass production, treatment of large areas, and strong anchoring energy. Because of the rubbing process, LC molecules on the polymer layer are oriented at a polar angle tilted away from the surface. The so-called pretilt angle is an important parameter in the design of LC devices because it has a marked influence on the electrooptic properties.

There have been many investigations on the pretilt angles on many different polymers and the mechanisms for generation of pretilt angles,¹¹ but so far no definitive understanding has been reached and relationships between the surface of PIs and the pretilt angles of LCs have been not fully understood. It was reported that the pretilt angle increases with the increase of the inclination angles of the PI chain.^{11,12} The pretilt angle with a certain nematic LC depends on the rubbing strength. Han and Uchida¹¹ proposed that the surface topology of a PI, after rubbing, is oriented in a certain tilted direction and angle, and an LC pretilt angle depends on the tilted angle of the PI film. It has been demonstrated that the optical second-harmonic generation (SHG) can be used to determine quantitatively the orientational distribution of a monolayer of molecules.¹² Application of the technique to the rubbed PI surfaces allows us to study how a surface can induce a bulk LC alignment.

In this work, several PIs were synthesized and characterized by Fourier transform infrared spectroscopy (FTIC) and thermogravimetric analysis. The relationships between the surface structures of PIs and helical or zigzag molecular chain conformations of the PIs were discussed. The effects of the molecular chain conformation of the PIs on the pretilt angles of LC molecules and the second-harmonic signals of the rubbed PI surfaces were also investigated in a systematic way.

EXPERIMENTAL

Materials

Pyromellitic dianhydride (PMDA), 3,4,3',4'-benzophenone tetracarboxylic dianhydride (BTDA), and 4,4'-(hexafluoroisopropylidene)diphthalic anhydride

(6FDA) were purchased from Tokyo Kasei Organic Chem. Co. 2,2-Bis[4-(4-aminophenoxy)phenyl]propane (BAPP), 2,2-bis[4-(4-aminophenoxy)phenyl]hexafluoropropane (BAPHF), bis[4-(4-aminophenoxy)phenyl]sulfone (BAPS), 1,4-bis(4-aminophenoxy)benzene (BAB), and 1,4-bis(4-aminophenoxy)biphenyl (BABP) were purchased from TCI Chem. Co. *N*-methyl-2-pyrrolidinone (NMP), *N,N*-dimethylacetamide (DMAc), and dimethylsulfoxide (DMSO) were purchased from Junsei Chemical Co., Ltd. Liquid crystal ZLI 1557 was purchased from E. Merck Industries. These chemicals were used as received.

Syntheses of PAA

The PAA precursors were prepared by the conventional solution polymerization methods in an aprotic solvent such as DMAc, NMP, or DMSO. The polymerizations were generally carried out in dry bottles equipped with stoppers and magnetic stirring bars. The dianhydrides were added in equimolar quantities to the diamines. Polymerization solutions were generally stirred at least overnight (16–24 h), then precipitated, filtered, dried, and stored in a refrigerator.^{13,14}

Preparation of Polyimides

In the first stage of the two-stage syntheses of aromatic PIs, PAA solutions are obtained by polycondensation of dianhydride with diamine in a polar aprotic solvent. Films formed from high-molecular-weight PAAs were dried at 80°C. The second stage of PI syntheses is imidization, in which the intrachain conversion of amic acid groups into imide rings takes place at 80 to 300°C. Table I lists the PAAs prepared in this work.

Preparation of Alignment Layers and Cells

PI films for alignment layers and cells were fabricated by spin-coating PAA solutions at 1000 rpm for 10 s and at 3500 rpm for 30 s on indium tin oxide (ITO)-coated glass substrates. The PI films were baked at 80°C and then cured at 150 or 250°C for 30 min at each temperature.¹⁵ Thickness of PI films was in the range of 600–800 Å. The PI-coated substrate was rubbed by a rubbing machine with a roller. The rubbing concentration was as follows: roller speed = 400 rpm, roller radius = 42 mm, speed of substrate stage = 11 mm/s, and rubbing depth = 0.3 mm, 0.5 mm. The nematic liquid crystal, ZLI 1557, was filled into

Table I Lists of the PIs Synthesized in This Work

Polyamic Acid	Notations	
	Dianhydride	Diamine
PMDA–BAPP	Pyromellitic dianhydride	2,2-Bis(4-(4-aminophenoxy)phenyl)propane
PMDA–BAPHF	Pyromellitic dianhydride	2,2-Bis(4-(4-aminophenoxy)phenyl)-hexafluoropropane
PMDA–BAPS	Pyromellitic dianhydride	Bis-(4-(4-aminophenoxy)phenyl)sulfone
PMDA–BAB	Pyromellitic dianhydride	1,4-Bis(4-aminophenoxy)benzene
PMDA–BABP	Pyromellitic dianhydride	1,4-Bis(4-aminophenoxy)biphenyl
BTDA–BAPP	3,4,3',4'-benzophenone tetracarboxylic dianhydride	2,2-Bis(4-(4-aminophenoxy)phenyl)propane
6FDA–BAPP	4,4'-(hexafluoroisopropylidene)-diphthalicanhydride	2,2-Bis(4-(4-aminophenoxy)phenyl)propane

cells under atmospheric pressure at room temperature and the cells were sealed. Thickness of the liquid crystal layer was in the range of 1.4–9 μm . The cell size was 3.5 \times 4 cm.

Thermogravimetric Analysis

Thermal stability was examined by a Schimadzu DT 30A thermogravimetric analyzer (TGA) at a scanning rate of 15°C/min under both nitrogen and air atmosphere.

Measurement of Contact Angle

The contact angle of water and methylene iodide on the surface of samples were measured by the Kyowa contact angle meter. The measurements were carried out in the presence of the saturated vapor of the probe liquids but the equilibrium pressure of the adsorbed vapor of the liquids on the polymer films was assumed to be negligible. The Young's harmonic-mean equation was applied to predict surface tensions from the contact angles of water and methylene iodide.¹⁶

Surface Morphology

Surface morphology was investigated on the basis of atomic force microscopy (AFM, Digital Instrument, Nanoscope IIIa).¹⁶ AFM images were obtained at room temperature. The AFM cantilever used was microfabricated from Si_3N_4 . AFM imaging was performed under a repulsive force, and the applied force to the microtip (force reference) was set between –0.021 or –0.088 nN (repulsive force) and 0.42 nN (attractive force).

Measurement of Pretilt Angle

The pretilt angle of uniform area was measured by the crystal rotation method. Thickness of cell

size for pretilt angle was 24–50 μm . Width of cell for pretilt angle was 3 \times 2.5 cm or 2 \times 3.5 cm. For a sample rotated by a motion controller, an exit polarizer and a photometer were used. The transmission axis of the polarizer was adjusted to make a 45° angle with respect to the projection of an LC detector. The axis of the exit polarizer was perpendicular to that of the polarizer. Transmission at an incident angle formed by rotation of the sample was rewarded on the photometer. Asymmetry offset angle was related to the pretilt angle, which was determined from a plot of transmission versus incident angle.

RESULTS AND DISCUSSION

Characterization

The FTIR analysis of PMDA–BAPP polyimide was employed to characterize the imidization by tracking the development of the characteristic imide band at approximately 1724 cm^{-1} (C=O, out-of-phase imide), 1383 cm^{-1} (CNC, axial-imide), and 725 cm^{-1} (CNC, out-of-plane bending imide).^{17,18} Table II shows the TGA data of PAAs and PIs. It is seen that all the polyimides containing diphenyl ether group are thermally stable up to about 550°C. The effect of the kinds of diamine and dianhydride was marginal.

Surface Tension and Polarity Before and After Rubbing

A harmonic-mean method utilizes the contact angle of two testing liquids and a harmonic-mean equation. The method is widely used to obtain the surface tension of a polymer, together with the liquid homolog method, the polymer melt method,

Table II Thermal Properties of Polyamic Acids and Polyimides Analyzed by TGA

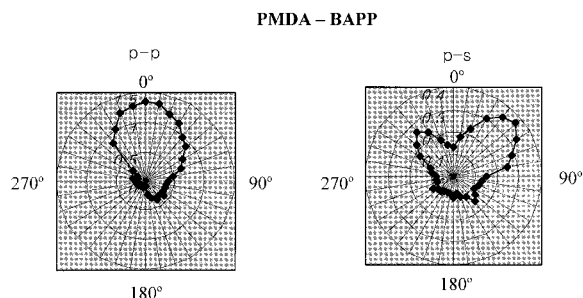
Samples	Temp. of 5% Weight Loss (°C)			Temp. of Decomposition (°C)		
	PI in		PI in N ₂	PI in		PI in N ₂
	PAA	Air		PAA	Air	
PMDA-BAPP	110	480	486	549	589	622
PMDA-BAPHF	124	500	525	548	551	598
PMDA-BAPS	102	447	509	572	598	617
PMDA-BAB	141	519	520	562	593	656
PMDA-BAB	110	485	500	577	583	633
BDTA-BAPP	103	533	550	552	572	621
6FDA-BAPP	101	541	548	612	579	620

and the equation of state method.¹⁶ Table III lists contact angles of water and methylene iodide for various polyimides and surface tensions obtained by the harmonic-mean method before and after rubbing. It is seen that the water contact angles measured after rubbing were reduced, regardless of the kind of PIs, indicating that the surface became much more polar. This is suggested to affect an electronic interaction between nematic LC molecules and the alignment layer surface, while the steric effect would be reduced. Both effects would cause the LC molecules to lie flatter.¹⁹ If an LC molecule does not contain a group to interact with the polar alignment surface, the electronic interaction will be negligible.

Table III Comparison of Surface Tension and Polarity as Determined by Harmonic-Mean Method (Surface Tension at 20°C, dyn/cm)

Polyimides	Contact Angle (deg)				Harmonic-Mean Method			
	Before Rubbing		After Rubbing		Before Rubbing		After Rubbing	
	θ_W	θ_M	θ_W	θ_M	γ	X^P	γ	X^P
PMDA-BAPP	73	23	70	19	48.9	0.245	50.7	0.262
PMDA-BAPHF	77	42	70	36	41.8	0.282	46.2	0.319
PMDA-BAPS	68	24	64	18	50.3	0.292	53.1	0.309
PMDA-BAB	69	21	66	18	50.6	0.275	52.3	0.293
PMDA-BABP	72	22	70	18	49.4	0.252	50.9	0.260
BTDA-BAPP	70	24	68	22	49.6	0.275	50.8	0.286
6FDA-BAPP	76	34	73	32	44.8	0.254	46.4	0.275

θ_W = contact angle of water; θ_M = contact angle of methylene iodide; γ = surface tension; γ^P = Polar Component of γ ; X^P = polarity $X^P = \gamma^P/\gamma$.

**Figure 1** The SHG signals of rubbed PMDA-BAPP before (p-p) and after (p-s) rubbing (rubbing depth, 0.3 mm; helical conformation).

Orientation Distribution of Surface Molecules

The rubbing treatment on the surface of polymers is the most common technique used in the LCD industry for controlling the LC alignment. SHG can be used to probe the morphology of a surface monolayer. This can be demonstrated by the observation of the SHG signal.¹⁹ The polymer-coated substrates were rubbed with a cloth. A rubbing treatment of the films orients polymer chains along a preferred direction and the molecular interaction between the LC molecules and the stretched polymer chain induces the alignment. Surface molecules after the rubbing treatment, with rubbing depth of 0.3 mm, were oriented to the direction of (rubbing 0°)(deg) (Figs. 1 and 2). Figures 1 and 2 illustrate typical SHG signals of rubbed PMDA-BAPP, whose chains adopt zigzag and planar conformations, and those

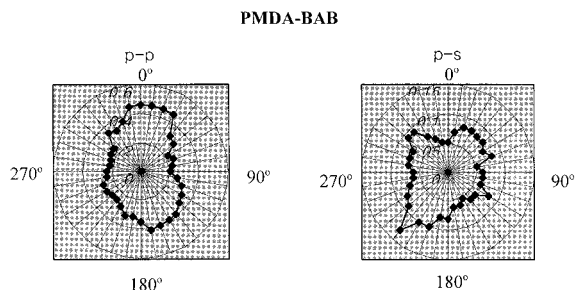


Figure 2 The SHG signals of rubbed PMDA-BAB before (p-p) and after (p-s) rubbing (rubbing depth, 0.3 mm; zigzag conformation).

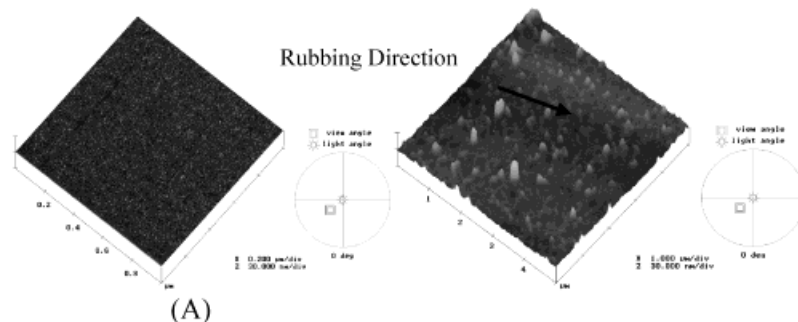
of PMDA-BAB, whose chains adopt helical and nonplanar conformations, respectively. The surface orientation of polyimides, PMDA-BAB and PMDA-BABP, whose chains adopt zigzag and planar conformations, were less improved by rubbing treatment than that of polyimides, PMDA-BAPP, PMDA-BAPS, and PMDA-BAPHF, whose chains adopt helical and nonplanar conformations, because the polyimide chains of zigzag and

planar conformation are easily packed.^{20–22} In Figure 3, the polar functionality has been measured by atomic force microscopy on the polymer alignment layer surfaces before and after rubbing treatment for both PMDA-BABP and PMDA-BAB. It was found that the rubbing treatment induced orientation of the polymer alignment layers surface (PALS), regardless of the chain conformations of PIs. It was reported by X-ray photoexcitation spectroscopic studies that carbonyl groups and ether groups are oriented to the direction of rubbing in general.²³

Effects of PI Chain Conformations on LC Pretilt Angles

The mechanical axis of a surface LC would form a certain angle with the alignment layer (AL) surface which in turn determines the tilt angle of bulk LCs. The observed tilt angle between LC molecules and the polymer surface is defined as a pretilt angle. Pretilt angles of LCs in contact with rubbed PI films that have different unit structures of the PI chains were measured by an im-

PMDA-BAPP



PMDA-BAB

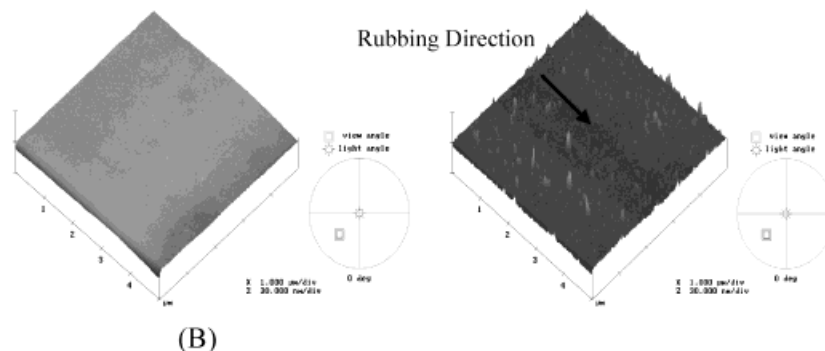


Figure 3 Atomic force micrographs of polyimide surface before (left) and after (right) rubbing. (A) Helical conformation; (B) zigzag conformation.

Table IV Pretilt Angles Measured by the Crystal Rotation Method

Polyimides	Pretilt Angle (°)	
	Rubbing Depth (0.3 mm)	Rubbing Depth (0.5 mm)
PMDA–BAPP	3.85	3.07
PMDA–BAPHF	4.35	3.67
PMDA–BAPS	2.08	1.86
PMDA–BAB	2.81	2.66
PMDA–BABP	2.11	1.95
BTDA–BAPP	3.25	2.56
6FDA–BAPP	2.05	1.64

proved crystal rotation method. Determining factors of LC pretilt angles are anchoring, steric, and electronic factors, whereas the rubbing strength and the cell gap are constant.

The anchoring factor includes tilted molecular structures of a PALS as well as the geometry of mesogens at the LC–AL interface.^{11,24,25} The two other factors are related to the interaction between LC molecules and the PALS. The third factor is the strength of electronic interactions. Polar surface gives a much smaller pretilt angle, which is an electronic factor. Hydrogen bonding, van der Waals, or dipole–dipole interaction between the LC molecules and the PALS also correspond to the electronic interaction. It has been known that the pretilt angle (θ_p) increases with the increase of the inclination angle (θ) of the PI chain.^{11,12} This result indicates that the pretilt angle is mainly determined by the inclination angle of the PI chain in the film. The repeating unit structure of the PI chain is the main factor determining the conformation of the PI chain and has influence on the inclination angle of the PI chain.

Table IV shows the pretilt angle data for two different rubbing depths (0.3 and 0.5 mm). As shown in Table IV, the polyimides, PMDA–BAPP and PMDA–BAPHF, whose chains adopt helical and nonplanar conformations, gave larger pretilt angles than the polyimides, PMDA–BAB and PMDA–BABP, whose chains adopt zigzag and planar conformations. It is considered that the propane and hexafluoropropane groups of the PMDA–BAPP and PMDA–BAPHF polyimides cause the PI chain conformations to be more nonplanar and give a steric effect on the LC molecules of ZLI 1557. However, the PMDA–BAPS PI whose chains adopt helical and nonplanar conformation gave smaller pretilt angle than the

PMDA–BAPP and PMDA–BAPHF polyimides. It can be explained that the sulfone groups in the polyimides cause the surface tension of its AL to be increased and give an electronic effect of hydrogen bonding on the LC molecules of ZLI 1557. The pretilt angles of polyimides, BTDA–BAPP and 6FDA–BAPP, with bridge groups and swivels in the diamine and the dianhydride residues, have to be determined by the combined factors of anchoring factor, steric factor, and electronic factor in consideration of the adjacency between bridge groups and swivels in the diamine and the dianhydride residues. The pretilt angles measured under the condition of rubbing depth of 0.5 mm were smaller than under the condition of rubbing depth of 0.3 mm. The result means that the strong rubbing treatment causes the whole molecular profile of the PALS to be flatter.^{26,27}

CONCLUSION

Several PAAs were synthesized and used for polycondensation with aromatic diamines to obtain various polyimides. It was analyzed that an imidization process occurred during heating from PAA to PI by FTIR and TGA. It was found that the thermal stability of PI containing diphenyl ether group was good. The decomposition temperatures of PI in air were in the range from 550 to 660°C.

The polar functionality has been measured by AFM on the PALS after rubbing treatment. The surface orientations of polyimides, PMDA–BAB and PMDA–BABP, whose chains adopt zigzag and planar conformations, were less improved by rubbing treatment than those of polyimides, PMDA–BAPP and PMDA–BAPHF, whose chains adopt helical and nonplanar conformations, because the polyimide chains of zigzag and planar conformation are easily packed. The polyimides, PMDA–BAPP and PMDA–BAPHF, whose chains adopt helical and nonpolar conformations, gave larger pretilt angles than the polyimides, PMDA–BAB and PMDA–BABP, whose chains adopt zigzag and planar conformations. However, the PMDA–BAPS polyimide whose chains adopt helical and nonplanar conformation gave smaller pretilt angle than the PMDA–BAPP and PMDA–BAPHF polyimides because of the electronic effect of hydrogen bonding. The pretilt angles of polyimides, BTDA–BAPP and 6FDA–BAPP, containing bridge groups and swivels in the diamine and the dianhydride residues, have to be deter-

mined by the combined factors of anchoring, steric factor, and electronic factor. The pretilt angles measured under the condition of rubbing depth of 0.5 mm were smaller than under the condition of rubbing depth of 0.3 mm.

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