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Synthesis and Properties of New Aromatic Polyimides – Polymeric Materials for Light-emitting and Liquid-crystal Displays

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SUMMARY: New aromatic diamines containing π-conjugated heterocyclic rings were synthesized, which emit blue light in the photoluminescence. Using these new monomers, soluble poly(amic acid)s were prepared by the polycondensations with pyromellitamic dianhydride, and thermally converted to the polyimides in films which emit intense blue-light. These polyimides are considered as potential candidate materials for fabricating optoelectronic devices which emit blue light. In addition, new poly(*m*-phenylene 4,4'-oxydiphthalimide)s containing various side chains were synthesized. For these polyimides, thermal properties were investigated with considering the chain flexibility of polymer backbone as well as the spacer and biphenyl mesogen end group in the side chains. In particular, these polyimides exhibited excellent performance in the rubbing process and the controlling of both the alignment and the pretilt of liquid-crystal (LC) molecules in the LC cell. This might be attributed mainly to a strong interaction between the biphenyl mesogen end group in the side chains and the mesogen unit of LC molecules.

Introduction

With increasing the usage of portable computers and telecommunication devices, there are highly demanded flat panel displays which have light weights and are operative with low power. Light-emitting display (LED) is counted as a good example of flat panel displays. A high performance light-emitting material is critical to fabricate LEDs. In particular, light-emitting polymeric materials have recently gained great attention because of their mass productionability and easy processability. Since a diode fabricated with poly(*p*-phenylenevinylene) (PPV) as the emitting layer was first reported to emit green light in 1990$^{1)}$, a number of polymeric materials suitable to LEDs have been developed. However, the most efficient polymeric systems are known to be based on PPV films, which emit basically green light rather than blue light (namely, one of the essential three light elements). There is still a big challenge in developing polymer systems to exhibit highly efficient blue-light emission, which can not be achieved easily from inorganic materials.

Another representative flat panel display is the liquid-crystal display (LCD). For full-color LCDs, polyimide films rubbed with a cloth are widely used to control the alignment of

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LCs in contact with the polymer film. In the case, LCs are known to be oriented in the rubbing direction. This phenomenon is directly related to the performance of LCDs, so that numerous research groups have involved to investigate its mechanism. However, the mechanism of aligning LCs at the rubbed polymer surface, especially at the rubbed surface of polymers with side chains, has been not understood fully, so that it is still one of the main subjects to be clarified in the field of LCDs.

In this study, 5,5'-bis(4-aminophenyl)-2,2'-bifuryl and 2,2'-bis(furyl)benzidine were synthesized, which are the new blue-light-emitting diamine monomers with well-defined conjugation lengths. Soluble poly(amic acid)s were synthesized by the polycondensations of these diamines with pyromellitic dianhydride. The soluble precursors then were thermally converted to the corresponding polyimides. The uv-visible absorption and fluorescence characteristics were investigated. And, the thermal stabilities were examined.

In addition, a series of new polyimide precursors were synthesized from 4,4'-oxydiphthalic anhydride and *m*-phenylene diamines containing various side chains. These side chains consist of a flexible alkyl chain spacer linked to various positions of the biphenyl mesogen end group which possibly plays together with LCs in the alignment. Thermal imidization behaviors of the precursor polymers were examined by thermogravimetry. The thermal properties were investigated by thermogravimetry, thermomechanical analysis and differential scanning calorimetry. And, the polyimide films were treated by rubbing with a cloth and used as alignment layers for constructing LC cells. In the LC cell, the pretilt characteristics of LCs were studied by crystal rotation technique as a function of rubbing density. All the results were understood with considering the role of mesogen end group and the side chain conformations and lengths in addition to the polymer backbone structure.

Experimental

Synthesis of monomers. 5,5'-Bis(4-aminophenyl)-2,2'-bifuryl (PFDA) was synthesized from 4-nitroaniline as a starting material, according to the synthetic scheme shown in Fig. 1. In the synthesis, *p*-nitrobenzenediazonium tetrafluoroborate **(1)** was obtained with a yield of 98.2 %: m.p., 161-167°C. **(1)** was reacted with furan, giving 2-(4-nitrophenyl)furan **(2)** in a yield of 63.2 %: m.p. 132-132.9°C. **(2)** was converted to bis(4-(2-furyl)phenyl)diazene **(3)** with 89.9 % yield: m.p. 249-251°C; ^{1}H NMR (δ, $CDCl_3$), 8.3 (dd, 4H, Ph-*H*), 7.75 (d, 4H, Ph-*H*), 7.5 (m, 2H, furyl-*H*), 6.7 (m, 2H, furyl-*H*), 6.5 (m, 2H, furyl-*H*). **(3)** was hydrogenated, producing **(4)** in a yield of 98 %: m.p. 156-157°C; ^{1}H NMR (δ, $CDCl_3$), 7.53 (d, 4H, Ph-*H*), 7.39 (dd, 2H, furyl-*H*), 6.86 (d, 4H, Ph-*H*), 6.4 (m, 4H, furyl-*H*), 5.7 (s, 2H, N*H*). (4) was rearranged to the diamine (PFDA): mass/e 316 (M^+); m.p. 203-205°C; ^{1}H NMR (δ, acetone-d_6), 7.5 (d, 4H, Ph-*H*), 6.72 (d, 4H, Ph-*H*), 6.68 (d, 2H, furyl-*H*), 6.62 (m, 2H, furyl-*H*), 4.88 (s, 4H,NH_2). Elemental anal. Calcd. for $C_{20}H_{16}N_2$: C, 75.93; H, 5.10; N, 8.86. Found: C, 75.68; H, 5.02; N, 9.04. Here, the product was obtained with a yield of 20 %.

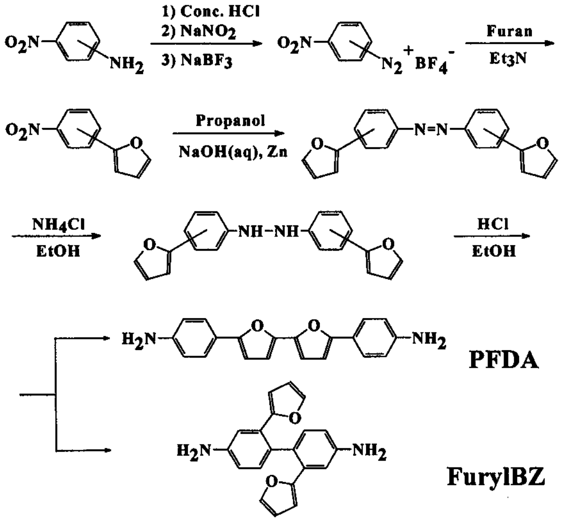

Fig. 1: Synthetic scheme of new blue-light-emitting monomers, 5,5'-bis(4-aminophenyl)-2,2'-bifuryl (PFDA) and 2,2'-bis(furyl)benzidine (FurylBZ).

2,2'-Bis(furyl)benzidine (FurylBZ) was also synthesized from 3-nitoaniline in the same manner as the PFDA was prepared: m.p. 156-157°C; ^{1}H NMR (δ, acetone-d_6), 7.37 (d, 2H, furyl-*H*), 7.25 (d, 2H, Ph-*H*), 6.84(d, 2H, Ph-*H*), 6.67 (dd, 2H, Ph-*H*), 6.17(dd, 2H, furyl-*H*), 5.42 (d, 2H, furyl-*H*), 4.78 (s, 4H,NH_2). Elemental anal. Calcd. for $C_{20}H_{16}N_2$: C, 75.93; H, 5.09; N, 8.85. Found: C, 75.71; H, 4.87; N, 9.50.

In addition, another four diamine monomers were newly prepared as follows. 6-(4-Phenylphenoxy)hexanol was derived from 6-bromohexanol and 4-phenylphenol in accordance to a method described in the literature$^{2)}$. In the same manner, there were prepared 6-(3-phenylphenoxy)hexanol, 6-(2-phenylphenoxy)hexanol, and 6-(4-biphenylmethoxy)hexanol. These hexanol derivatives were substituted to 2,4-dinitrofluorobenzene by the etherification as reported previously in the literature$^{3)}$. The obtained dinitrobenzene derivatives were converted to the corresponding diamines: 2,4-diamino-(6-(4-phenylphenoxy)-hexyloxy)benzene (BP1), 2,4-diamino-(6-(3-phenylphenoxy)hexyloxy)benzene (BM1), 2,4-diamino-(6-(2-phenylphenoxy)hexyloxy)benzene (BO1), and 2,4-diamino-(6-(4-biphenylmethoxy)hexyloxy)benzene (BP2).

Synthesis of poly(amic acid)s and polyimides. The purified pyromellitic dianhydride (PMDA) of 1.3970 g (7.390 mmol) was added slowly to the PFDA of 2.3358 g (7.390 mmol) dissolved in 36 mL *N*-methyl-2-pyrrolidone (NMP) with stirring vigorously in a glove box filled with dry nitrogen gas (see Fig. 2). Once the dianhydride addition was completed, the reaction flask was capped tightly and stirring was continued for 1 day to make the polymerization mixture completely homogeneous, finally giving a poly(amic acid) (PAA) solution, PMDA-PFDA PAA. In the same manner, PMDA-FurylBZ PAA was prepared in NMP from PMDA and FurylBZ monomers.

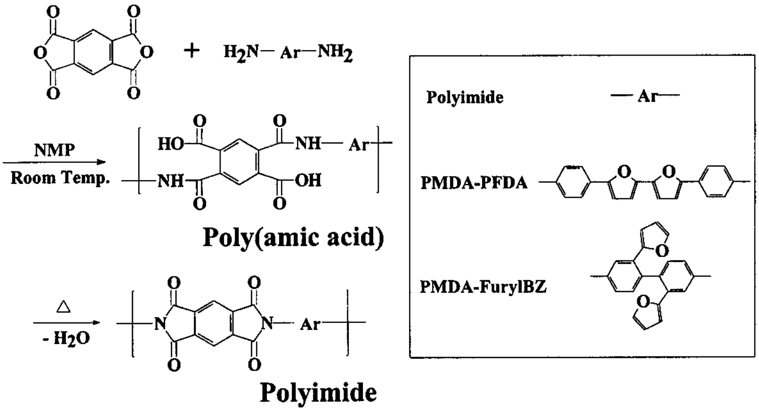

Fig. 2: Synthetic scheme of soluble poly(amic acid)s and polyimides from pyromellitic dianhydride (PMDA) with 5,5'-bis(4-aminophenyl)-2,2'-bifuryl (PFDA) and 2,2'-bis(furyl)-benzidine (FurylBZ).

Another series of PAA precursors were synthesized in NMP by the polycondensations of 4,4'-oxydiphthalic anhydride (ODPA) with *m*-phenylene diamine (MPD) and its derivatives containing short side chains, such as BP1, BM1, BO1, and BP2: ODPA-MPD PAA, ODPA-BP1, ODPA-BM1 PAA, ODPA-BO1 PAA, and ODPA-BP2 PAA (see Fig. 3).

Solid contents of the PAA precursor solutions were 8-12 wt.%. These solutions were filtered with silver metal membranes of 1.0 μm pore size, tightly sealed, and stored in a refrigerator of -4°C before use. For these precursor polymers, the intrinsic viscosity [η] was measured in NMP at 25.0°C using an Ubbelohde suspended level capillary viscometer as a method described in the literature[4,5]: 0.661 dL/g for PMDA-PFDA PAA, 0.545 dL/g for PMDA-FurylBZ PAA, 0.207 dL/g for the ODPA-BP1 PAA, 0.259 dL/g for the ODPA-BM1 PAA, 0.653 dL/g for the ODPA-BO1 PAA, 0.245 dL/g for the ODPA-BP2 PAA, and 0.400 dL/g for the ODPA-MPD PAA.

The PAA solutions were spin-coated on glass substrates, followed by soft-baking on a hot plate at 80°C for 1 h. The soft-baked precursor films were thermally imidized in an oven with a dried nitrogen gas flow by a three-step protocol: 150°C/30 min, 230°C/30 min, and 300°C/60 min. A ramping rate was 2.0 K/min for the first two steps and 5.0 K/min for the final step. After imidization, the samples were cooled to room temperature with a rate of 10.0 K/min. The thickness of the obtained polyimide (PI) films was in the range of 3-20 μm. The films were taken off from the glass substrates with the aid of deionized water, followed by drying for 2 days at 50°C in a vacuum of 5×10^{-4} torr. For measurements of physical properties, films were cut into appropriate sizes. In addition, for uv-visible spectroscopic measurements, polyimide films of 0.1-2 μm thickness were prepared on quartz substrates from a diluted solution (1-2 wt.% solid content) of the poly(amic acid).

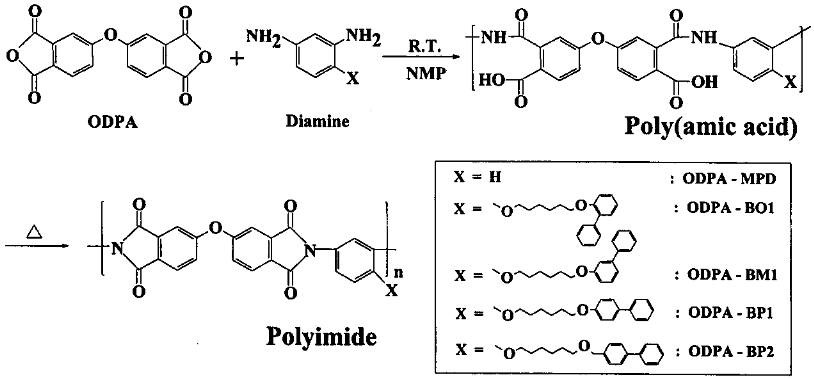

Fig. 3: Synthetic scheme of poly(amic acid)s and polyimides from ODPA and diamines with various side chains.

Characterization. The product obtained at each synthetic step was identified by ^{1}H NMR spectroscopy. ^{1}H NMR spectra were measured using a Bruker ASPECT 300 MHz NMR spectrometer in acetone-d_6 or chloroform-d_1 solvent. Melting points were determined using a Thomas Hoover capillary melting point apparatus. In addition, for the newly synthesized diamine monomer, the molecular weight was determined using a mass spectrometer (Hewlett-Packard HP-5970) coupled with a gas chromatographic analyzer (Hewlett-Packard HP-5890). Elemental analysis was carried out using an Elemental Vario analyzer.

Thermogravimetric analysis (TGA) was carried out for the soft-baked poly(amic acid)s and their polyimide using a Perkin-Elmer thermogravimeter (Model TGA7) under a dry nitrogen gas flow. That is, a baked precursor sample was heated up to 300°C with a rate of 5.0 K/min, then soaked at 300°C for 1 h, and finally cooled to 50°C. Then, the imidized sample was again heated up to 800°C with a ramping rate of 5.0 K/min.

Glass transition temperatures (T_g's) were measured over 25-400°C using a Seiko differential scanning calorimeter (Model DSC-220CU). During the measurement, dry nitrogen gas was purged with a flow rate of 80 cc/min and a ramping rate of 10.0 K/min was employed.

In scanning run, a sample of about 5 mg was used. The temperature calibration was carried out using indium and tin, and the enthalpy calibration using indium. T_g was taken as the onset temperature of glass transition. In-plane thermal expansion coefficients (TECs) were measured with a load of 5 g at a ramping rate of 5.0 K/min over the range of 50-150°C under a nitrogen gas flow using a Seiko thermomechanical analyzer (Model TMA-120 CU) with a tension probe. The gauge length was 20.0 mm and the width of film strips was 2 mm. For each film strip, the measured TECs were averaged out over the range of 70-120°C.

For the new PFDA and FurylBZ monomers and their polyimides, excitation and photoluminescence spectra were measured at room temperature using a fluorescence spectrophotometer (Shimadzu RF-500) with a Xenon lamp. For both excitation and emission monochromators, bandpasses were 2 nm, respectively. Photoluminescence behavior of the new monomer was investigated for its solution with a concentration of 1.5×10^{-5} g/mL in 1,4-dioxane. The excitation wavelength employed was 340 nm. On the other hand, the polyimide in films was excited with a wavelength of 380 nm in a front-face arrangement in order to minimize the self-absorption. The size of polyimide specimens was 10 x 30 mm. UV-visible spectroscopic measurements were performed using a Hewlett-Packard spectrometer (Model HP-8452A).

In addition, relative fluorescence quantum yield (Φ_f) of the diamine monomer was measured in 1,4-dioxane by comparing the ratio of fluorescence emission intensity maximum to uv absorbance at the excitation wavelength used for the sample with that of a standard, quinine sulfate6-9). For the polyimide in films, Φ_f was determined by the comparison with *N,N'*-dicyclohexylperylenebisimide dye dispersed in poly(methyl methacrylate)10).

Some of polyimide films coated on substrates were rubbed with varying rubbing density (L/*l*)11,12) using a laboratory rubbing machine with a roller covered by a rayon cloth (Yoshikawa Company, YA-20-R): $L/l = N[(2\pi rn/60v) - 1]$ where L is the total length (mm) of the rubbing cloth which contacts a certain point of the polymer film, *l* is the contact length (mm) of circumference of rubbing roller, *N* is the cumulative number of rubbings, *n* is the speed (rpm) of rubbing roller, *r* is the radius (cm) of roller, and *v* is the velocity (cm/s) of the substrate stage. Here, the thickness of polyimide films used as alignment layers was in the range of 4.0-5.0 μm.

Two pieces of the rubbed substrates were assembled together in the anti-parallel rubbing direction by using 50 μm thick poly(ethylene terephthalate) film spacers. A nematic LC, 4-*n*-pentyl-4'-cyanobiphenyl (5CB) was injected into the cell gap, followed by sealing the injection hole with an epoxy glue. Then, pretilt angle (α) of the LC molecules was measured using a crystal rotation apparatus which was made in our laboratory12).

Results and Discussion

Synthesis

PFDA and FurylBZ monomers were synthesized from 4-nitroaniline and 3-nitroaniline, respecively, by the five-step reaction sequence as shown in Fig. 1. Depending on the nitroaniline isomers, the reaction yield was 97-99 % at the first-step, 63-64 % at the second-step, 55-90 % at the third-step, 98 % at the fourth-step, and 20-21 % at the fifth-step. In comparison, the final step gave the lowest product yield. The low yield was attributed to possibly many side reactions occurred in the benzidine rearrangement reaction.

Phenylphenoxyhexanol isomers were synthesized with yields of 45-59 % from the reactions of 6-bromohexanol with three isomeric phenylphenols. In addition, 6-(4-biphenylmethoxy)hexanol was prepared with a yield of 53-54 % from 6-bromohexanol and 4-biphenylmethanol. Here, before reacting with phenylphenol isomers, 6-bromohexanol was protected with 3,4-dihydro-2*H*-pyran which could be deprotected in mild acidic condition, in order to avoid the reaction between its hydroxy and bromide group. The obtained phenylphenoxyhexanol isomers were further reacted with 2,4-dinitrofluorobenzene, respectively, leading to 2,4-dinitrobenzenes with four different side chain analogs consisting of a flexible spacer and a biphenyl mesogen. Yields of these coupling reactions were 89-92 %. The obtained dinitrobenzene derivatives were reduced to the corresponding diamine monomers: the yields were 42-47 %. These low yields might be due to dissociation reactions of the ether linkages in the relatively strong acid condition. However, the diamine products were successfully purified by column chromatography with silica gel. Through the whole reaction steps, the total yield was 18-25 %, depending on the diamine derivatives.

Using the newly synthesized diamine monomers, various poly(amic acid)s were prepared in NMP by the conventional low temperature polycondensations with PMDA and ODPA monomers. All the soluble poly(amic acid)s were obtained with reasonably high molecular weights: the intrinsic viscosity [η] was in the range of 0.400-0.661 dL/g, depending upon the poly(amic acid)s. Some of PAA precursors had relatively low [η] values (0.207-0.259 dL/g) but gave a good quality of films in the formation of polyimide films.

Imidization and thermal properties

The prepared poly(amic acid) solutions were spin-cast on glass substrates, followed by soft-baking at 80°C. For the soft-baked PAA films, thermal imidization was performed under a dry nitrogen atmosphere by thermogravimetry (TGA). In the heating run, the weight dropped sharply over 100-186°C, which is due to the removal of residual NMP solvent as well as the byproduct (that is water) of imidization in part. The further weight loss occurred over 186-300°C, due to the removal of the byproduct as well as the continuous removal of residual solvent. Then, the weight loss levels off during soaking for 1 h at the final imidization temperature, 300°C.

For polyimides prepared by imidization at 300°C, thermal stability was examined under a dry nitrogen atmosphere by TGA. The PMDA-PFDA PI film was stable up to ca. 370°C and then gradually degraded until ca. 520°C. Thereafter, the rate of the weight loss is significantly increased with increasing temperature. A similar TGA thermogram was obtained for the PMDA-FurylBZ PI. However, the polymer was stable up to ca. 400°C.

The ODPA-MPD PI without any side group was stable up to 480°C and began to degrade with increasing temperature. The polymer shows a small weight loss over the range of 480-620°C and then a large weight loss above 620°C: that is, the polyimide apparently reveals a two-step weight loss behavior. However, the suggested two-step degradation mode needs to be further investigated in details for full understanding. In comparison, the side chain containing polyimides show distinct two-step weight loss behaviors: the weight loss at the first-step might be due to the degradation of side groups and that at the second-step due to the degradation of polyimide main chain. In conclusion, the incorporation of side groups reduces the thermal stability of ODPA-MPD PI. In comparison, the thermal stability is in the decreasing order ODPA-MPD PI (T_d = ca. 480°C) > ODPA-BP1 PI (ca. 400°C) ≈ ODPA-BM1 PI ≈ ODPA-BO1 PI > ODPA-BP2 (ca. 330°C): here, T_d is the onset temperature of degradation.

In addition, in-plane thermal expansion coefficient (TEC) and glass transition temperature (T_g) were measured for the polyimides. The ODPA-MPD PI without side chain exhibited 33 ppm/°C TEC and 271.4°C T_g. However, all the side chain containing polyimides revealed relatively high TECs and low T_gs. TEC and T_g were 68 ppm/°C and 150.4°C for ODPA-BP1, 65 ppm/°C and 140.5°C for ODPA-BM1, 69 ppm/°C and 139.3°C for ODPA-BO1, and 58 ppm/°C and 148.5°C for ODBP2 PI, respectively. Conclusively, both TEC and T_g of ODPA-MPD PI are reduced by incorporating side chains. For the side chain containing polyimides considered, their TEC varies further with the flexible spacer length and its conformation, whereas the T_g changes further with the isomeric structure of biphenyl group.

Light-emitting characteristics

For the PFDA and FurylBZ solutions in 1,4-dioxane (1.5 x 10^{-5} g/mL), the uv-visible spectra exhibited broad featureless absorptions with the lowest energy absorption maximum at 376 nm and 326 nm, respectively. These absorptions are considered to be the π-π^* transition, leading to the formation of singlet excitons. With this UV-visible absorbance characteristic, the monomer solutions were excited at a wavelength of 340 nm, which provide the best fluorescence spectra. The solutions exhibited a strong emission peak centered at 442-443 nm, regardless of the isomeric structures. The relative fluorescence quantum yield (Φ_f) was measured to be Φ_f = 92 % for the PFDA and Φ_f = 52 % for the FurylBZ. Conclusively, these new diamine compounds emit an intense blue fluorescence.

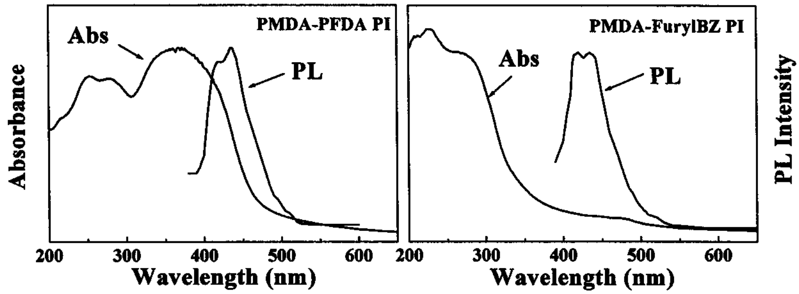

Fig. 4: UV-visible absorption (Abs) and photoluminescence (PL) spectra of the polyimide films, which were imidized at 300°C for 1 h: the film thickness was 0.6 μm for the measurement of UV-visible spectrum and 15.5 μm for the measurement of PL spectrum. The excitation was at 380 nm.

On the other hand, the PMDA-PFDA PI film exhibited a very broad featureless absorption at < 470 nm, while the PMDA-PFDA PI film showed a very broad featureless absorption at < 400 nm (see Fig. 4). When the PI films were excited at 380 nm, the best emission spectra were obtained. As shown in Fig. 4, the measured emission spectra are very similar to those of the PFDA and FurylBZ solutions, respectively. However, each PI film showed an emission peak having two peak maxima rather than a single peak maximum: 419 nm and 436 nm for the PMDA-PFDA PI; 419 nm and 435 nm for the PMDA-FurylBz PI. The two peaks in the emission spectrum of each PI film may be a vibronic structure instead of two separate peaks. In comparison, the emission spectrum of each PI film is relatively broader than that of its diamine monomer. This may result mainly from the nature of vibronic structure in the emission spectrum. However, the emission spectra of these PI films still are relatively much narrower than those of other light-emitting polymers, such as poly(*p*-phenylenevinylene) and its copolymers$^{1,6,13\text{-}16)}$. The Φ_f was measured to be 1.2 % for the PMDA-PFDA PI and 7.4 % for PMDA-FurylBZ PI. The Φ_fs are much higher than that (9.7 x 10^{-7}) of poly(4,4'-oxydiphenylene pyromellitimide)$^{17)}$ which is the representative of conventional polyimides. In particular, the Φ_f of PMDA-FurylBZ PI is comparable to that (0.085-0.115) of poly(2-methoxy-5-(2'-ethyl)hexyloxy-*p*-phenylenevinylene)$^{18)}$ (that is, an analog of PPV) which emits orange light. However, the PMDA-PFDA PI has a relatively low Φ_f value, compared to the PMDA-FurylBZ PI. This might be attributed to the ordered structure in the PMDA-PFDA PI film, which is evident in the X-ray diffraction pattern.

Alignment of LC molecules

The polyimide films were rubbed with varying rubbing density. For the rubbed polyimide films, the formation of microgrooves on the surface was confirmed to be in the rubbing direction by atomic force microscopy. The rubbed polyimide films were used to make LC cells as alignment layers. For the LC cells filled with 5CB molecules which are a nematic LC, the pretilt angle (α) of LCs was measured by the crystal rotation technique as a function of rubbing density. The results are presented in Fig. 5.

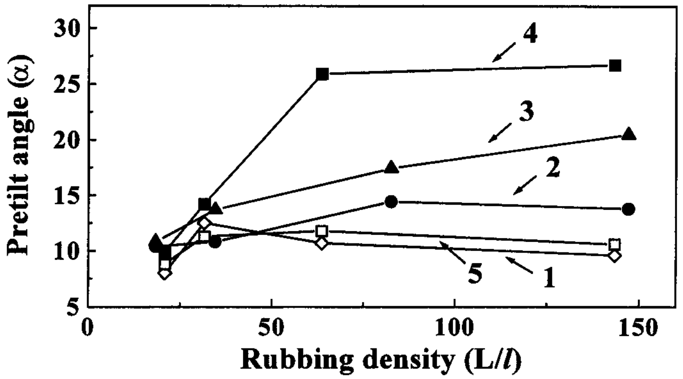

Fig. 5: Variations of the pretilt angle of LC (5CB) molecules in contact with the rubbed surfaces of polyimide films as a function of rubbing density (L/*l*): 1, ODPA-BP2 PI; 2, ODPA-BO1 PI; 3, ODPA-BM1 PI; 4, ODPA-BP1 PI; 5, ODPA-MPD PI.

For the LC cell fabricated with the ODPA-MPD PI film, the α of LC molecules increased initially with increasing rubbing density, but leveled off at ca. 31.5 rubbing density. Otherwise, the α decreased slightly over the high rubbing density range of > 63.6. A maximum α of 11.8° was achieved at a rubbing density of 63.6. This α value is relatively larger than those (0.7-5.1°) achieved for the 5CB filled LC cells fabricated with various polyimides without side chains[12,19)]. The α value is comparable to those (13.0-14.0°) for the LC cells fabricated by some other polyimides with and without long alkyl side chains[19)]. Similar results were obtained for the LC cells prepared with the ODPA-BP2 PI and ODPA-BO1 PI. However, the α values were achieved in high level, compared to the ODPA-MPD PI.

Different from the PIs discussed above, both ODPA-BM1 PI and ODPA-BP1 PI gave very large α values in the LC cells. For the LC cell with ODPA-BM1 PI, the α increased continuously with increasing rubbing density over the range of rubbing density (< 150) considered in the present study: that is, the α value varied in the range of 10.8-20.5° over < 150 rubbing density. For the LC cell fabricated with ODPA-BP1 PI, the α increased with rubbing density and leveled off at 63.6 rubbing density. Thereafter, the α further increased very slowly with rubbing density. An extremely large α of 26.0-27.0° was achieved over $\geq$ 63.6 rubbing density. In comparison, an achievable maximum pretilt angle is in the increasing order ODPA-MPD $\leq$ ODPA-BP2 < ODPA-BO1 << ODPA-BM1 < ODPA-BP1.

Conclusions

New PFDA and FurylBZ monomers emitting highly intense blue lights were synthesized, and their polyimides were prepared by the polycondensation reactions with PMDA and subsequent thermal imidization. The monomers, as well as their polyimide films were characterized by photospectrometry. The polyimides in films also emitted blue lights as detected for the monomers. The polymers were thermally stable up to 370-400°C. Conclusively, these polymers are considered as potential candidate materials for fabricating optoelectronic devices including LEDs which can emit blue light.

MPD derivatives having three different isomeric 6-(phenylphenoxy)hexyloxy groups as well as 6-(4-biphenylmethoxy)hexyloxy group as side chains were newly synthesized. Using these monomers, a series of polymers were synthesized by the polycondensations with ODPA and subsequent thermal imidization. These polymers were thermally stable up to 330-480°C, depending upon the side groups as well as the length of flexible spacers in the side group. In addition, T_gs and TECs were determined: by incorporating side chains, the TEC was increased and the T_g was decreased.

In addition, all the polyimides exhibited excellent performance in the rubbing process and the controlling of the alignment of LC molecules in the LC cell. The rubbing process with a relatively low rubbing density of 30-85 provided these polyimides an excellent controllability to pretilt LC molecules properly and to align LC molecules highly in the rubbing direction, which are highly desired in the LCD industry. The LC molecules were aligned well in the rubbing direction even by rubbing with a low rubbing density. The pretilt angle of LC molecules was achieved in a wide angle range of 8-27°, depending upon the rubbing density as well as the sort of polyimides. The pretilting behavior of LC molecules on the rubbed surface were very sensitive to all the molecular parameters in addition to the rubbing process. That is, a high flexibility of and a highly random orientation of polymer chains cause the LC molecules to pretilt with a relatively high angle. And, the conformation of flexible spacer and the isomeric structure of biphenyl mesogen end group in the side chain involve highly in controlling the pretilt of LC molecules. For the side chain containing polyimides studied here, the 6-(phenylphenoxy)hexyloxy and 6-(4-biphenylmethoxy)hexyloxy side chains, which are much shorter in length than the long alkyl side chains in the polyimides being used widely as LC alignment layers, were evident to involve effectively in the alignment of and the pretilt of LC molecules which are highly desired in the LCD industry. In particular, the major role of these side chains in pretilting LC molecules in a proper way might be attributed mainly to a strong interaction between the biphenyl mesogen end group and the mesogen unit of LC molecules. In conclusion, all the short side branched polymers have good properties suitable for applications in LCDs as well as microelectronic devices.

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References

1) J. H. Burroughes et al., *Nature* **347**, 539 (1990)
2) N. Miyashita, A. Yoshikoshi, and P. A. Grieco, *J. Org. Chem.*, **42**, 3772 (1977)
3) T. Ichino et al., *J. Polym. Sci.: Part A: Polym. Chem.*, **28**, 323 (1990)
4) S. I. Kim, S. M. Pyo, K. Kim, M. Ree, *Polymer* **39**, 6489 (1998)
5) S. I. Kim, S. M. Pyo, M. Ree, *Macromolecules* **30**, 7890 (1997)
6) A. Hilberer, H.-J. Brouwer, B.-J. V. D. Scheer, J. Wildeman, G. Hadziioannou, *Macromolecules* **28**, *28*, 4525 (1995)
7) J. C. Phelan, C. S. P. Sung, *Macaromolecules* **30**, 6837 (1997)
8) J. N. Demas, G. A. Crosby, *J. Phys. Chem.* **75**, 991 (1971)
9) W. H. Melhuish, *J. Phys. Chem.* **65**, 229 (1961)
10) M. Hasegawa, Y. Shindo, T. Sugimura, S. Ohshima, K. Horie, M. Kochi, R. Yokota, I. Mita, *J. Polym. Sci.: Part B: Polym. Phys.* **31**, 1617 (1993)
11) T. Uchida, M. Hirano, and H. Sakai, *Liquid Crystal*, **5**, 1127 (1989)
12) S. I. Kim, S. M. Pyo, M. Ree, M. Park, and Y. Kim, *Mol. Cryst. Liq. Cryst.*, **316**, 209 (1998)
13) Z. Yang, I. Sokolik, F. E. Karasz, *Macromolecules* **26**, 1188 (1993)
14) Z. Yang, F. E. Karasz, H. J. Geise, *Macromolecules* **26**, *26*, 6570 (1993)
15) D.-H. Hwang et al., *Bulln. Korean. Chem. Soc.* **16**, 35 (1995)
16) T. Zyung et al., *Chem. Mater.* **7**, 1499 (1995)
17) G. Arjavalingam, G. Hougham, J. P. Lafemina, *Polymer* **31**, 840 (1990)
18) J. C. de Mello, H. F. Wittmann, R. H. Friend, *Adv. Materials* **9**, 230 (1997)
19) K.-W. Lee, S.-H. Paek, A. Lien, C. During, and H. Fukuro, *Macromolecules*, **29**, 8894 (1996)