Magromolegular Research

Volume 14, Number 1 February 28, 2006

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Review

High Performance Polyimides for Applications in Microelectronics and Flat Panel Displays

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Received September 14, 2005; Revised November 29, 2005

Abstract: Polyimides (PIs) exhibit excellent thermal stability, mechanical, dielectric, and chemical resistance properties due to their heterocyclic imide rings and aromatic rings on the backbone. Due to these advantageous properties, PIs have found diverse applications in industry. Most PIs are insoluble because of the nature of the high chemical resistance. Thus, they are generally used as a soluble precursor polymer, which forms complexes with solvent molecules, and then finally converts to the corresponding polyimides via imidization reaction. This complexation with solvent has caused severe difficulty in the characterization of the precursor polymers. However, significant progress has recently been made on the detailed characterization of PI precursors and their imidization reaction. On the other hand, much research effort has been exerted to reduce the dielectric constant of PIs, as demanded in the microelectronics industry, through chemical modifications, as well as to develop high performance, light-emitting PIs and liquid crystal (LC) alignment layer PIs with both rubbing and rubbing-free processibility, which are desired in the flat-panel display industry. This article reviews this recent research progresses in characterizing PIs and their precursors and in developing low dielectric constant, light-emitting, and LC alignment layer PIs.

Keywords: polyimide, polyimide precursor, imidization, structure, properties, orientation, surface morphology, interaction, applications.

Introduction

Poly(4,4'-oxydiphenylene pyromellitimide) (PMDA-ODA PI) was first commercialized in early 1960s.^{1,2} Thereafter, a number of polyimides (PIs) have been synthesized and investigated extensively in aspects of structure and property relationships and applications.³⁻⁵² In general, PIs are known to be thermally stable due to its heterocyclic imide rings on

the backbone, and the thermal stability is further siginficantly improved by incorporating aromatic rings on the backbone and/or side groups. In addition to such high thermal stability, the nature of the chemical structure consisting rigid imide and aromatic rings always provides excellent mechanical and dielectric properties as well as high chemical resistance. Beyond these advantageous properties, a variety of functionalities (for examples, photoreactivity, molecular recognition ability, nonlinear optical responsibility, lightemit ability, and so on) can be added into the backbone and/

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or side groups of PIs, depending on their demands in applications.²²⁻⁸⁸ Due to these advantageous properties as well as the functionalities, PIs have found diverse applications in the microelectronics, flat panel display, aerospace, and chemical and environmental industries as flexible circuitry carriers, stress buffers, interdielectric layers, passivation layers, liquid crystal alignment layers, varnishing resins, fibers, matrix materials, and gas and chemical separation membranes.²²⁻⁸⁸ This article explores recent research progresses in developing high performance PIs for applications in the microelectronics and flat panel displays, as well as in characterizing their structure, chain orientation and properties.

Processability

PIs are generally classified as soluble and nonsoluble polymers depending on their solubilities.3-8,13-52,61-71,83-106 A few soluble aliphatic and aromatic PIs have been reported so far.63,74 Most aromatic polyimides cannot be processed because they are insoluble and have a high glass transition temperature.^{3-8,13-52,61-71,83-106} Thus, they are first synthesized in a soluble precursor form and then processed in various ways, before finally being converted to PIs.^{3-8,13-52,61-71,83-106} Poly(amic acid) (PAA) and poly(amic dialkyl ester) (PAE) are representative soluble precursors, which are soluble in N-methyl-2-pyrrolidone (NMP), dimethyl sulfoxide, and N,N-dimethylacetamine. PAA and PAE are usually processed first as a specific form depending on applications and then imidized either thermally or chemically. The processabilities of PIs can be further improved depending on their photoreactivities.48,63,64,74-82 Photoreactive PIs can be directly patterned by conventional lithographic process,48,63,64,74-82 while non-photoreactive PIs can be patterned by lithographic process with the aid of photoresists.53-55

Glass Transition Behaviors of PI Precursors

As mentioned above, PAAs have been widely used as a representative processable precursor due to their good solubilities in organic solvents.^{3-8,13-52,61-71,83-106} In spite of the wide usages as well as the detailed characterizations of their imidized products, the glass transitions in the PAA precursors could not be measured yet. There are two main difficulties in the measuring glass transition temperature T_{p} of a PAA with solvent free. First, PAA precursor forms complexes with dipolar aprotic solvents through strong interaction between the orthoamic acid groups of the precursor polymers and the basic solvent molecules, so that it is very difficult to remove all solvent molecules from the cast PAA specimen. Each orthoamic acid group of the PAA precursor in a dipolar aprotic solvent, for example NMP, is known to complex with the solvent molecules. For this complex formation, dried PAA specimen still contains typically >20 wt% of NMP,

depending on the drying conditions. The residual solvent significantly reduces T_g of the PAA and, furthermore, influences the imidization kinetics severely. Second, PAA precursor is expected to exhibit a relatively high T_g due to its relatively high chain rigidity. Over the T_g range or below, it undergoes imidization and converts to the corresponding PI. PAA is known to start imidization reaction around 130 °C, and the imidization reaction is accelerated with increasing temperature.¹⁰⁷⁻¹¹⁰ In general, the glass transition of PAA is overlapped with or higher than the imidization temperature.

Recently, it was attempted to measure glass transition behaviors of some PAA specimens by using a new differential calorimetric technique, oscillating differential calorimetry (ODSC): poly(4,4'-oxydiphenylene pyromellitamic acid) (PMDA-ODA PAA), poly(p-phenylene oxydiphthalamic acid) (ODPA-PDA PAA), and poly(p-phenylene benzophenonetetracarboxamic acid) (BTDA-PDA PAA).¹¹¹ In addition, the amounts of residual solvents in the precursor polymer specimens were measured by proton nuclear magnetic resonance (¹H-NMR) spectroscopy.¹¹¹ For a given PAA precursor, T_g was measured with varying the content of residual solvent.¹¹¹ The T_g s of the PAAs in solvent free were estimated by best fitting of the measured T_{gs} with a modified Gordon-Taylor equation.¹¹¹ The estimated true T_g s were interpreted with considering the chain rigidity and rotational freedoms along the chemical bonds.¹¹¹ In addition, a phase diagram was constructed for the PMDA-ODA PAA/NMP mixture system.¹¹¹

Tiny pieces of a PMDA-ODA precursor sample softbaked at 80 °C for 1 h were dissolved in dimethyl- d_6 sulfoxide (DMSO- d_6) and characterized by ¹H-NMR spectroscopy. The amount of NMP solvent in weight fraction was estimated from the peak integrations of the measured ¹H-NMR spectrum. The content of residual NMP in the dried film was determined to be 47.0 wt%. Thus, the content of the precursor polymer was 53.0 wt%. For precursor samples dried at the other conditions, NMP and polymer contents were determined in the same manner. This characterization was extended to both ODPA-PDA and BTDA-PDA precursor samples dried at various conditions.

For these highly dried precursor samples, all the residual NMP molecules are assumed to participate in forming complexes with the orthoamic acid groups of the precursors, so that the number of NMP molecules bound to the repeat units of the precursors can be estimated from the contents of residual solvent measured by NMR spectroscopy. The number of NMP molecules bound per the chemical repeat unit of precursor is calculated to be 1.7 for the PMDA-ODA, 1.4 for the ODPA-PDA, and 1.5 for the BTDA-ODA precursor.

A BPDA-PDA PAA sample with a residual NMP of 28.5 wt% was characterized by conventional DSC and by ODSC. As shown in Figure 1, the heat flow curve of glass transition could not be recognizable on the conventional DSC thermogram, because the endothermic heat flow due



Figure 1. The conventional DSC thermogram of a PMDA-ODA PAA sample containing 28.5 wt% residual NMP solvent. A heating rate of 10.0 °C/min was employed.

to the imidization is predominant over the temperature range of 100-250 °C. Thus, only the imidization behavior of the precursor sample can be observable from the conventional DSC thermogram.

In contrast, Figure 2(a) shows the oscillating input temperature signals as well as the ODSC output signals as a function of time. The ODSC thermogram can be nicely separated into two parts, the specific heat flow and the kinetic heat flow. The separated specific and kinetic heat flows are plotted in Figure 2(b) as a function of temperature. The specific heat flow curve reveals clearly glass transition over 110-150 °C. From this thermogram, T_g was determined to be 119.5 °C for the dried precursor sample: Here, T_{p} is defined as the onset temperature of glass transition in the specific heat flow. On the other hand, the kinetic heat signal curve shows a broad, big endothermic heat flow peak which results from the imidization reaction and the removals of the reaction byproduct (i.e., water) and residual solvent. The onset temperature of imidization (T_i) in the dried film was estimated to be 139.1 °C. The ODSC measurement was extended to the other PMDA-ODA precursor samples dried at various conditions. As the content of residual NMP in the precursor sample reduced to 28.5 wt% from 47.0 wt%, T_{a} increased to 119.5 °C from -6.0 °C and T_i also increased to 139.1 °C from 118.4 °C. Overall, the residual NMP in the precursor sample caused significant reductions in both glass transition and imidization temperatures. However, the effect of residual NMP is relatively more significant in the T_g than the T_i . The ODSC investigation was also carried out for the PMDA-ODA PAA samples contained >50 wt% NMP, including NMP itself as well as the precursor solution with a concentration of 10.9 wt%. These samples exhibited melting transition or glass transition at the temperature region much lower than the imidization temperature. For this fact, measurements were carried out in the conventional mode. The melting point (T_m) of the pure NMP was -23.6 °C: Here,



Figure 2. (a) The input temperature signal and output ODSC signal of a PMDA-ODA PAA sample containing 28.5 wt% residual NMP solvent; a heating rate of $10.0 \,^{\circ}$ C/min was employed; the temperature amplitude and frequency used in the oscillation were $10.0 \,^{\circ}$ C and $0.02 \,$ Hz, respectively. (b) The signals of specific and kinetic heat flow component separated from the ODSC thermogram in (a).

 T_m is defined as the temperature of the peak maximum of NMP melting in the conventional DSC signal. For these NMP rich mixtures, T_m of the NMP component was depressed, depending on the content of precursor polymer. T_m was depressed to -27.9 °C for the precursor solution itself with 10.9 wt% precursor, -32.1 °C for the sample with 21.8 wt% precursor, and -29.8 °C for the sample with 37.7 wt% precursor.

In addition, from these T_g and T_m data with varying compositions, a phase diagram was constructed for the PMDA-ODA PAA/NMP mixture. The result is illustrated in Figure 3. For the NMP rich mixture, the T_m of the NMP component was almost linearly depressed with increasing the precursor content, whereas for the precursor rich mixture the T_g of the precursor component was convexly depressed with increasing the solvent content. They are extrapolated to meet together at the composition of 51.7 wt% NMP and 48.3 wt% precursor. Here, in the NMP rich region, *regime* I, the dashed



Figure 3. The variation of glass transition temperature T_g or melting point T_m of PMDA-ODA precursor/NMP solvent mixture as a function of precursor weight fraction. The symbols denote the measured phase transition temperatures. The solid curve is the curve fitted by a modified Gorden-Taylor equation from the T_g data measured in the *regime* II.

line was generated from the linear fitting of the measured T_m s in the precursor rich region, *regime* II, the solid curve was made by best fitting of the measured T_g s with a modified Gordon-Taylor equation.^{112,113} The phase behaviors in the *regime* II is described further in the latter part.

Both ODPA-PDA and BTDA-PDA precursors in the dried state were characterized by ODSC in the same manner as the PMDA-ODA precursor samples were investigated. For all the ODSC thermograms, the specific heat flow parts were separated from the kinetic heat flow parts. Both T_{gs} and T_{i} s were estimated from the separated specific and kinetic heat flow curves, respectively.

Here, it was attempted to estimate true T_g s of the PAA precursors, namely, T_g s of the precursors in solvent free from the T_g s measured for the precursor/NMP mixtures. For all the PAA/NMP mixtures T_g variations with composition are convex particularly in the precursor rich region, *regime* II.

In fact, the type of T_g -composition profile in a miscible mixture is known to depend strongly upon the interaction nature between the components. Both the linear and concave relationships indicate that the blend components interact together via mainly van der Waals attraction, leading to the miscible blends. The convex relationship is known to result from strong intermolecular interactions, such as hydrogen bonding, acid-base interaction, and charge complexation, between the blend components.

Therefore, in this study the modified Gordon-Taylor expression was adapted in order to illustrate convex T_g variations with composition observed for all the three PAAs contained residual NMP solvent via strong acid-base complexation between the orthoamic acid group of the polymers and the secondary amino group of the NMP molecules and, furthermore, to estimate their true T_g s in solvent free.

For the PMDA-ODA PAA/NMP mixture in the *regime* II, the measured T_{gs} were best fitted, resulting in $T_{g} = 207.4$ °C for the PMDA-ODA precursor in solvent free. This analysis was extended for the ODPA-PDA and BTDA-PDA precursors in only the *regime* II regions. The estimated true T_{g} was 166.3 °C for the ODPA-PDA and 213.2 °C for the BTDA-PDA precursor. In comparison, the true T_{g} increases in the order ODPA-PDA < PMDA-ODA < BTDA-PDA precursor. Overall, all the precursors exhibit T_{gs} higher than the onset temperatures in their imidizations.

In general, T_g of a polymer is strongly dependent upon the chain rigidity. Thus, chain rigidities of the PAA precursors were attempted to be estimated here. Kuhn statistical segment length $(L_K)^{114}$ is known to be a measure of chain rigidity. Although Kuhn statistical segment length does not provide all about the chain rigidity, it can give some information about the chain rigidity. For the reason, Kuhn statistical segment lengths of the precursor polymers were estimated in accordance to a calculation procedure reported previously.¹¹⁵ The calculation was carried out with three assumptions in the following. First, the amide linkage in the repeat unit of a PAA possesses a planar trans-structure.¹¹⁵ Second, in the PAAs all the backbone skeletal valence angles, such as \angle C_{ar} -C-N, \angle C-N- C_{ar} , \angle C_{ar}-O- C_{ar} , and \angle C_{ar}-C- C_{ar} are equally to be 120°.116 Finally, the precursors are alternatively linked by their possible isomeric repeat units. For PMDA-ODA PAA, the chemical repeat units have two diff-erent isomeric structures: meta and para isomeric units. For both ODPA-PDA PAA and BTDA-PDA PAA precursors, the chemical repeat units have four different isomeric structures: metapara, meta-meta, para-para, and para-meta isomeric units.

The calculated L_K was 43.3 Å for the PMDA-ODA PAA and 34.6 Å for both the ODPA-PDA PAA and the BTDA-PDA PAA. That is, chain rigidity is in the decreasing order PMDA-ODA PAA > ODPA-PDA PAA≈BTDA-PDA PAA. These chain rigidities may be directly related to the T_{g} s: In general, higher chain rigidity produces higher T_g . Therefore, from the estimated L_K , T_g is expected to be in the decreasing order PMDA-ODA PAA > ODPA-PDA PAA≈BTDA-PDA PAA. This expection is in good agreement with the experimental results for PMDA-ODA PAA and ODPA-PDA PAA. However, BTDA-PDA PAA exhibited higher T_g than that of ODPA-PDA PAA although its L_K was estimated to be same with that of ODPA-PDA PAA. Furthermore, its T_{g} is higher than that of PMDA-ODA PAA even though its L_K is smaller than that of PMDA-ODA PAA. This is evidence that the L_K in the BTDA-PDA PAA was underestimated. This may result from two reasons as follows. First, for the BTDA-PDA PAA, the rotational freedom along the Car-C-Car linkage seems to be resticted by the oxygen atom of the carbonyl linkage which makes π -conjugations with the linked aromatic carbons, forming a coplanar structure with the linked phenyl rings. The limited rotational freedom in the BTDA-PDA PAA repeat unit causes a reduction in the overall chain flexibility, consequently leading to an increase in its T_g . Second, the conjugation with carbonyl may affect the proportions of isomeric units, increasing the chain rigidity.

The ODSC analysis was extended for PAE precursors, which have recently gained great attention from the industry because of their high hydrolytic stability due to the absence of monomer-precursor polymer equilibration, providing a processability more adequate to the device fabrication:^{50,52,117} poly(4,4'-oxydiphenylene biphenyltetracarboxamic diethyl ester) (BPDA-ODA PAE), poly(*p*-phenylene biphenyltetracarboxamic diethyl ester) (BPDA-ODA PAE), poly(*p*-phenylene biphenyltetracarboxamic diethyl ester) (BPDA-PDA PAE), poly(*p*-phenylene biphenyltetracarboxamic diethyl ester) (BPDA-PDA PAE), poly(4,4'-oxydiphenylene pyromellitamic diethyl ester) (PMDA-ODA PAE), and poly(*p*-phenylene pyromellitamic diethyl ester) (PMDA-PDA PAE).¹¹⁷

For the precursors in powders, both BPDA-ODA PAE and PMDA-ODA PAE revealed T_g but the others did not show T_g .¹¹⁷ However, T_g was detectable for all the precursors in films.¹¹⁷ This result might come from the morphological differences caused by the sample preparation processes. The glassy state might be highly disturbed in the powder samples, resulting in a relatively very small heat capacity change through the glass transition. In contrast, the glassy state might be relatively developed well in the film samples, and its heat capacity change through the glass transition is reasonably large, allowing the detection of its T_{p} . The measured T_{gs} are in the range of 179.2-235.4 °C, depending upon the precursor backbone structure as well as the history of sample preparation. These T_{g} s are very close to their T_{i} s, causing difficulties in the T_g measurements: $\Delta T (= T_i - T_g)$ is in the range of -1.7 °C to 24.3 °C, depending upon the precursor backbone chemistry and the history of sample preparation. The measured T_i s are in the range of 198.1-225.2 °C for the powder samples and of 213.7-235.4 °C for the film samples, depending upon the sort of precursors. For the precursors except PMDA-PDA PAE, higher chain rigidity reveals higher T_{e} and higher T_{i} . The T_{i} s are shown to be further influenced by the morphological variation caused by sample preparation processes, whereas the T_i s are observed to be further affected by both the chemical nature of precursor and the morphological variation caused by sample preparation processes.

Imidization Behaviors of PI Precursors

PAA Precursor. For PIs prepared from PAA precursors, the morphological structure and properties have been found to strongly depend on the imidization history.^{3-63,64-88} However, structural analyses have been mostly limited to the morphological structures of polyimides that have already been prepared under particular conditions.^{3-5,22-56,119,120} Even study of the imidization behavior of PAAs has been limited mostly to polymer samples that had already been imidized. Various

thermal analysis techniques have been employed, such as thermogravimetry (TGA), conventional DSC and ODSC, and dynamic mechanical thermal analysis, to examine the in-situ imidization behavior of PAA precursors.^{6,13,107-111,121} However, each chemical repeat unit in PAAs contains carboxylic acid and amide groups, which can form complexes with solvent molecules via hydrogen bonding as described in a previous section. Hence, PAAs always contain some amount of residual solvent as described in the previous section. Such residual solvent molecules are evaporated together with the water byproduct generated by imidization. This situation makes it difficult to use thermal analysis techniques to quantitatively determine the imidization behavior of PAA. In contrast, Fourier-transform infrared (FTIR) spectroscopy avoids such difficulties, and has therefore been widely used as a powerful tool for investigating the imidization behavior of PAAs.¹⁰⁻¹² In spite of the advantages of IR spectroscopic analysis, it has been restricted to polyimides that were already prepared from PAAs. Furthermore, previous works on characterizing structural and imidization behavior have focused mainly on only a few polyimide systems, such as PMDA-4,4'-ODA PI and BPDA-PDA PI.6,10-13,107-111,121

The *time-resolved* measurement of the structural evolution during the imidization of PAA precursor has yet to be conducted. A study of this type is critical to determining the mechanism of the structural formation of polyimide, and to further understanding the relationship between structure and properties. Imidization behavior has not been previously studied on a *time-resolved* basis, which is essential to understanding polyimide formation and resultant structure and properties.

Poly(3,4'-oxydiphenylene pyromellitamic acid) (PMDA-3,4-ODA PAA) was chosen because it is another representative PAA precursor, and its thermal imidization behavior was investigated in detail using TGA and *time-resolved* FTIR spectroscopy.^{122,123}

TGA was conducted on the dried PAA films of thickness 3.5 μ m that contained 32.0 wt% NMP. A typical TGA thermogram is illustrated in Figure 4, which gives the weight loss and its first derivative measured while heating the PAA film. The PAA displays a three-step weight loss behavior below 380 °C. The first step appears below 123 °C and involves a relatively small weight loss, which is probably due to the decomplexation of NMP molecules bound via hydrogen-bonding to the amide linkages and carboxylic acid groups of the PAA precursor chains. The second step occurs over the temperature range 123-202 °C, and involves a large and rapid weight loss. This significant weight loss might be due to the removal of the decomplexed NMP solvent and the water byproduct of the imide-ring closures of the PAA polymer chains being imidized. In addition, the minimum in the plot of d(Weight)/dT versus T appears at 142.5 °C, indicating that the highest rate of weight loss occurs at that temperature. The third step occurs over the range 202-380°C,



Figure 4. TGA thermogram and its first derivative for PMDA-3,4'-ODA PAA. The measurement was conducted under nitrogen atmosphere. The heating rate was 2.0 °C/min until 380 °C and thereafter 5.0 °C/min.

and shows a very small weight loss with a slow rate, which might result from the dehydration of the partially imidized precursor chains that are still undergoing imide-ring closure with a slow imidization rate.

Beyond the three steps of weight loss described above, another significant weight loss appears in the temperature region higher than 516.4 °C, which is due to the decomposition of the imidized polymer chains.

From the results it is concluded that in the heating run the PAA precursor simultaneously commences both decomplexation from NMP molecules and imidization at around 123 °C, and then undergoes the majority of imidization over the range 123-202 °C, but the completion of imidization requires thermal heating to > 202 °C.

Time-resolved FTIR spectroscopic investigation was carried out during the thermal imidization of the precursor film under the same conditions as the TGA measurement described above.

Figure 5(a) shows typical IR spectra taken at three different temperatures during imidization. Some characteristic IR peaks can be assigned in these spectra with the aid of previously reported results for PMDA-4,4'-ODA PAA and its PI and model compounds,^{10,11} as well as and BPDA-PDA PAA and its PI.¹¹⁰

In the spectrum of the PAA precursor measured at 80 °C, the peak centered at 1722 cm⁻¹ is assigned to the stretching of the carbonyl (-CO-) in the carboxylic acid group, while the peak centered at 1662 cm⁻¹ is assigned to the vibrational characteristics of amide-I (i.e. stretching of the carbonyl (-CO-) in the amide linkage). The two peaks at 1545 cm⁻¹ and 1536 cm⁻¹ are assigned to the vibrational characteristics of amide-II (-CNH- bend-stretch). In addition, the two peaks at 1508 and 1489 cm⁻¹ are assigned to the ring-breathing modes of the *para-* and *meta*-substituted benzene rings in



Figure 5. IR spectra measured during thermal imidization of PMDA-3,4'-ODA PAA at a rate of 2.0 °C/min. Part (a) shows the IR spectra measured at the indicated temperatures on the heating run. Part (b) displays typical IR spectra monitored during the imidization as a function of temperature. Part (c) shows vibrational characteristics of amide-II (-CNH- bend-stretch) and aromatic ring (ring-breath) monitored over 30-230 °C as a function of temperature.

the 3,4'-ODA unit, respectively. Lastly, the peak at 1597 cm⁻¹ corresponds to the quadrant stretch of carbon-to-carbon double bonds in the aromatic ring, which overlaps in part

with the vibrational peaks of amide-I.

On the other hand, for the spectrum of the imidized polymer at 380 °C, the two peaks at 1774 and 1725 cm⁻¹ are assigned to the in-phase and out-of-phase stretching vibrations of the imide carbonyl (-CO-), respectively. The single peak at 1363 cm⁻¹ is assigned to the -CN- stretch in the imide-ring, while another peak at 722 cm⁻¹ is assigned to the bending mode of the carbonyl in the imide-ring. In addition, both the aromatic ring-breathing modes and the quadrant stretch of -C=C-, which are observed in the PAA precursor, are detected in the polyimide. The asymmetric stretch of -COC- in the 3,4'-ODA unit is clearly detected at 1231 cm⁻¹.

Figure 5(b) illustrates representative IR spectra measured in situ during the imidization of the PAA precursor. In the imidization run, the characteristic peaks of amic acid groups (carboxylic acid, amide-I, and amide-II) vary slightly with temperature even before the imidization reaction begins. However, when the imidization reaction begins, these vibrational peaks decrease drastically with increasing temperature, while the characteristic peaks of the imide ring appear and become stronger with increasing temperature. In order to quantitatively investigate the imidization behavior of the PAA precursor, the following characteristic peaks have been separated from each IR spectrum and their peak areas plotted as a function of temperature: amide-II and anhydride carbonyls as well as imide carbonyl and -CN- linkage. The estimated peak maxima and peak areas, normalized to their respective maximum values, are plotted in Figure 6 as a function of temperature. These plots are discussed in detail in the following.

Figure 6(a) shows the temperature dependence of the amide-II peak area. The drastic drop in area over 124-210 °C is attributed to the consumption of amide linkages by imidering formation. This indicates that the imidization reaction takes place mainly in the temperature range 124-210 °C in the heating run. The amide-II peak is still detected up to 310 °C, although its intensity is very weak. This indicates that the imidization reaction continues until 310 °C.

In addition, a small drop in the amide-II peak is observed in the range 70-110 °C, where imidization is not yet involved. The amide-II feature appears as two vibrational peaks rather than a single peak (see Figure 5(c)). The two peaks vary with temperature. For the dried precursor film, a main peak is observed at 1545 cm⁻¹ with a shoulder peak at 1536 cm⁻¹. However, on elevating the temperature to 100 °C, the high frequency peak weakens whereas the low frequency peak becomes more intense. The two peaks reach almost equivalent intensity at 100 °C, and maintain that level up to 124 °C. When the imidization reaction takes place above 124 °C, the high frequency peak weakens further, becoming a shoulder, and the low frequency peak strengthens, becoming the main peak. The overall intensity of the two peaks decreases with elevating temperature because of the conversion of amide linkages to imide rings.



124 °C

,6000000000

Amide-II

400

(a)

1.0

0.8

0.6

vibrational bands measured during thermal imidization of PMDA-3,4'-ODA PAA at a rate of 2.0 °C/min. Part (a) shows the temperature dependence of the amide-II (-CNH- bend-stretch) peak area. Part (b) displays variations of the vibrational peaks of the imide ring as a function of temperature: -, $V_a(CO)$ (-CO- out-of-phase stretch); \Box , v_s (CO) (-CO- in-phase stretch); \triangle , δ (CO) (-CObend); \bigcirc , ν (C-N) (-C-N- stretch).

In fact, the amide linkage in PAA has been found to form complexes with residual NMP solvent⁷¹ and other amic acid groups both intra- and inter-molecularly^{111,124,125} via hydrogen-bonding. In the heating run, residual NMP molecules are evaporated out continuously with increasing temperature. Furthermore, such hydrogen-bonds weaken with elevating temperature because they are in equilibrium with their constituents. Thus, the two amide-II peaks, as well as their intensity variations, originate from the complexation process of amide linkages with residual NMP molecules and other amic acid groups. The high frequency peak is due to amide linkages complexed with NMP molecules and other amic acid groups, whereas the low frequency peak results from amide linkages that are for the most part free from NMP and other amic acid groups. Conclusively, the intensity drop in the range 70-100 °C is caused by the complexation-todecomplexation transition of amide linkages with NMP and other amic acid groups, and subsequent NMP evaporation. Furthermore, amide linkages undergo imidization through a two-step process, decomplexation from NMP and other amic acid groups followed by imide-ring closure.

Figure 6(b) illustrates both the -CN- stretch and -CO- bend of the imide-ring, which vary with temperature. These bands first appear at 124 °C, after which their peak intensities rapidly increase with increasing temperature up to 210 °C. Thereafter, they slowly increase, reaching their maximum values at 310 °C. Similarly, the -CO- in-phase stretching peak of the imide ring first appears at 106 °C, after which its peak intensity increases drastically with increasing temperature up to 210 °C before slowly reaching its maximum at 310 °C. In addition, the -CO- out-of-phase stretching peak of the imide-ring shows similar behavior in the peak area versus temperature plot to that observed for its in-phase stretching peak. However, it is noteworthy how the analysis of the peak was done. This peak in the imide-ring overlaps fully with the stretching vibration of carbonyl in the carboxylic acid group of the PAA precursor. Thus, the initial peak area measured at 30 °C is subtracted from all the measured peak areas.

Above 310 °C the peaks of both the -CN- stretch and the -CO- bend decrease slowly with increasing temperature, while the -CO- in-phase stretching peak drops substantially as the temperature is raised. In contrast, the -CO- out-ofphase stretching peak increases with temperature. These variations may be due to a temperature dependence in their absorption coefficients, or to their orientations with respect to the film plane. The orientation effect arises because the samples were monitored in transmission mode in the IR measurement in which the electric vector of the IR beam is in the film plane. In addition, it is well known that rigid and semi-rigid aromatic polyimides in thin films exhibit large out-of-plane birefringence due to their high in-plane orientations taken place through imidization process.^{6,10-12,121} Such in-plane chain orientation may occur favorably in the thin film of the PMDA-3,4'-ODA PAA precursor which undergoes imidization because of semi-rigid chain characteristic of the resulting polyimide. Indeed both the -CN- and the -CO- vibrations monitored in this study might be influenced by in-plane orientation of the polymer chains occurred in the thin film. The -CO- bond of the imide-ring is a side group, whereas the -CN- bond is a part of the backbone, causing the -CO- stretching and bending peaks to be sensitive to orientation of the imide-ring itself, compared to the -CN- stretching peak. Here it, however, is noted that the axes of -CN- bonds in the in-plane oriented polyimide chain are not necessary to be parallel to the polymer chain axis, because the polyimide having one ether linkage per chemical repeat unit on the backbone is a kink polymer chain rather than a fully rodlike one. Taking into account these aspects, the variations of the -CN- and -CO- vibrational peaks observed above 310 °C reflect that the state of molecular orientation gradually changes further above that temperature.

As described above, one may use all five vibrational peaks from the amide-II and imide-ring to determine the degree of imidization (see Figure 6). However, the -CNH- bendstretching peak of amide-II is sensitive to the content of residual solvent, because it is affected by complexation with the solvent. Furthermore, this peak is influenced by hydrogen-bonding with other amide and carboxylic acid groups. Such complexation and hydrogen-bonding are influenced by temperature, causing the stretching peak to be changed further by variations in the temperature. These factors cause some errors in the determination of the peak area, which is critical for estimating the degree of imidization. On the other hand, the imide carbonyl peak in the out-of-phase stretching mode overlaps fully with the carbonyl stretching peak in the carboxylic acid of the PAA precursor, as mentioned above. In addition, both in-phase stretching and bending peaks in the imide carbonyl overlap in part with those of the carbonyl of the anhydride group that forms transiently during the heating run. The formation of the anhydride group is discussed in detail below. These carbonyl peaks may change further, depending on the in-plane orientation of the imidering in the thin film. All of the factors mentioned above cause errors in the estimation of the peak intensities and areas.

In contrast, the stretching peak of -CN- in the imide-ring is free from overlap with other peaks and is less sensitive to in-plane orientation of the imide ring. Monitoring the imide -CN- peak therefore proved to be the most valuable way of determining the degree of imidization.

The degree of imidization ($X_{Imidization}$) was determined from the plot of the imide -CN- peak versus temperature. As illustrated Figure 7, the precursor film starts to imidize at 124 °C and has undergone 93.5% imidization by 210 °C, finally reaching 100% imidization at 310 °C. If any small amount of precursor chains or unimidized segments remains, they should undergo imidization upon further heating to 380 °C and soaking at that temperature.



Figure 7. Degree of imidization and its derivative as estimated from the variation of the imide -CN- stretching band measured during thermal imidization of PMDA-3,4'-ODA PAA at a rate of 2.0°C/min.

Figure 7 presents a plot of $d(X_{Imidization})/dT$ versus T, which shows a maximum at 148.4 °C. This indicates that the imidization reaction takes place with a maximum rate at that temperature. As mentioned above, the weight loss with temperature in the TGA thermogram gives the maximum rate of weight loss at 142.5 °C. These results suggest the followings. First, the imidization process in the precursor is closely related to its decomplexation from residual NMP molecules and other amic acid groups. The decomplexed NMP molecules evaporate from the film sample, apparently leading to a maximum rate of weight loss at 142.5 °C. Second, the decomplexation and evaporation of residual NMP molecules immediately initiates and accelerates the imidization of the precursor polymers, and the imidization proceeds with a maximum rate at 148.4 °C. In addition, the evaporation of water byproduct generated by the imidization contributes to the weight loss. Finally, the decomplexed solvent molecules may act as plasticizers in the polymer film until they evaporate out. Such plasticization makes the precursor polymer chains more mobile, facilitating their imidization.

PAE Precursor. PAE precursor is representative of another type of soluble PI precursors.^{16,50,52,126,-129} PAE has better solubility than PAA, as well as higher hydrolytic stability due to the absence of the carboxylic acid groups that cause monomer-polymer equilibration in solution.^{16,50,52,126,-129} Moreover, films of PAE can be produced that are free of residual solvent, which means that there is no reduction in thickness of the film that is associated with the removal of residual solvent in the PI film formation process. For these reasons, PAE has recently gained increased attention from industry.^{16,50,52,126,-129} Despite this interest in PAE, its imidization behavior and resulting properties, which are essential to understanding PI formation and the structure and properties of the polymer, have rarely been investigated in detail.

PAE films that are free of residual solvent can be used to enhance our understanding of imidization, because the complexities that result from the presence of solvent molecules bound to the precursor, as observed for the PAA precursor, are avoided. This property of PAE enables the detailed investigation of its imidization behavior and imidizationinduced structure and property relationships.

Therefore, we chose PMDA-3,4'-ODA PAE as our model PAE precursor, and then investigated its thermal imidization behavior in microscale thin films using TGA and *time-resolved* FTIR spectroscopy.¹³⁰

A typical TGA thermogram is illustrated in Figure 8, which gives the weight loss and its first derivative measured while heating the PAE film. In the TGA run, the PAE power displays a three-step weight loss behavior below 390 °C. The first step appears below 220.8 °C and involves 1.1% weight loss, which is probably due to the H₂O or trapped residual NMP molecules in a small amount. The second step occurs over the temperature range 220.8-300.6 °C, and involves a large and rapid weight loss. This significant weight loss is



Figure 8. TGA thermogram and its first derivative for PMDA-3,4'-ODA PAE. The measurement was conducted under nitrogen atmosphere. The heating rate was 2.0°C/min until 400°C and thereafter 5.0°C/min.

due to the removal of C₂H₃OH byproduct generated by the imide-ring closure reaction of the PAE precursor. In addition, the minimum in the plot of d(Weight)/dT versus T appears at 253.7 °C, indicating that the highest rate of weight loss occurs at that temperature. The third step occurs over the range 300.6-387.5 °C, and shows a small weight loss with a slow rate, which might result from the removal of C₂H₅OH of the partially imidized precursor chains that are still undergoing imide-ring closure with a slow imidization rate. Beyond the three steps of weight loss described above, another significant weight loss appears in the temperature region higher than 540.6 °C, which is due to the decomposition of the imidized polymer chains.

The time-resolved FTIR spectroscopic measurements were carried out during the thermal treatment of the PAE precursor film. Figure 9 shows the IR absorption spectra of a film of the PAE precursor in-situ monitored over the range 1200-1830 cm⁻¹ during heating up to 400 °C at a rate of 2.0 °C/min. In these spectra, some characteristic IR peaks can be assigned with the aid of previously reported results for PAA precursors, their PIs and model compounds.^{10-12,122-125}

In the spectrum of the PAE precursor obtained at 30 °C, the absorption peak centered at 1662 cm⁻¹ is assigned to the characteristic vibration of amide-I, namely carbonyl (-C=O-) stretching in the amide linkage, and the double peaks at 1540 cm⁻¹ are assigned to vibrations of amide-II, namely -CNH- bend-stretch vibrations. The single peak at 1363 cm⁻¹ is assigned to characteristic imide -CN- stretching in the imide-ring. Taking these IR peak assignments into account, the in-situ monitored IR spectra in Figure 9 show that during the heating run the characteristic amide peaks vary little with increasing temperature below 216 °C and then drastically decrease in intensity with further increases in the intensity of the amide peaks above 216 °C are attributed to the



Figure 9. FTIR spectra of a microscale film of PMDA-3,4'-ODA PAE precursor measured over the range 1200-1830 cm⁻¹ during thermal imidization with a heating rate of 2.0 °C/min over the range 30-400 °C.



Figure 10. Degree of imidization and its derivative as estimated from the variation of the imide -CN- stretching band measured during thermal imidization of PMDA-3,4'-ODA PAE at a rate of 2.0 °C/min.

consumption of the amide linkages by imide-ring formation. Other the other hand, the imide peak appears for the first time around 216 °C and then becomes stronger with further increases in temperature, indicating the formation of imide-rings above 216 °C. These results indicate that the imidization reaction takes place mainly above 216 °C during the heating run. Taking these results into account, the imide peak at 1363 cm⁻¹ was chosen from the assigned IR peaks and used for estimating the $X_{Imidization}$ as a function of temperature. The variation of the degree of imidization with temperature is shown in Figure 10.

As can be seen in Figure 10, the PAE precursor film starts to imidize at 216 °C and has undergone 99% imidization by

356 °C, finally reaching 100% imidization above that temperature. This progression of thermal imidization is quite different from those of PAA precursors in films.^{10-13,103,108-111,118,122-125} Figure 10 also presents a plot of $d(X_{Imidization})/dT$ versus *T*; the maximum at 256 °C indicates that the imidization reaction takes place with a maximum rate at that temperature. At this temperature, the maximum imidization rate is much higher than those observed for films of PAA precursors.^{122,123}

PI Dielectrics

PIs are known to reveal relatively low dielectric constant (low-k), which ranges 2.6-3.0, depending on the chemical compositions.¹⁻¹³¹ These k values are considerably lower than those of today's workhorse dielectrics silicon dioxide (k=3.9-4.3) and silicon nitride (k=6.0-7.0), but are still much higher than that of air (k=1.01) or vacuum (k=1.00), which is the lowest value attainable. Low-k dielectrics have received significant attention from the microelectronics industry and end users because their use in integrated circuits (ICs) with multilayer structures can lower line-to-line noise in interconnects and alleviate power dissipation issues by reducing the capacitance between the interconnect conductor lines. Further, low-k dielectrics have advantages over low-resistivity metal conductors such as copper and silver, because in addition to providing device speed improvements they also provide lower resistance-capacitance delay.^{1-7,15,16,131} Thus low-k dielectric materials are in high demand in the microelectronics industry, which is rapidly developing advanced ICs with multilayer structures that have improved functionality and speed in a smaller package and that consume less power.^{1-7,15,16,131} Apart from having a low k value, dielectric materials must meet the thermal stability requirements of the metallization processing of ICs. The metallization process is conducted at temperatures below 250 °C but are usually followed by thermal annealing in the range 400-450 °C to ensure the production of void-free metal deposits. Thus, dielectric materials must be able to withstand this temperature for several hours. Further, dielectric materials have high mechanical modulus and toughness, low thermal expansion coefficient, and low interfacial stress.

Linear, aromatic PI dielectrics generally reveal higher molecular packing coefficient, providing higher mechanical modulus as well as low thermal expansion coefficient and low interfacial stress.^{8,89,90,132-134} Such high property performances are achievable from fully rodlike poly(*p*-phenylene pyromellitimide) (PMDA-PDA PI) and poly(4,4'-biphenylene pyromellitimide) (PMDA-BZ PI), so that they are so attractive to both industry and academia. However, they are very brittle and further their dielectric constants are not low enough, so that they are practically useless. Thus, there still is a big challenge to improve their brittleness and dielectric constant with retaining the high moduli. Attempts to improve such drawbacks with a little sacrifice of the high modulus have been made in two different ways: (i) incorporation of short side groups into the polymer backbone⁸⁹⁻⁹⁹ and (ii) insertion of proper linkages into the polymer backbone.⁶

There are two options in incorporating short side groups into the polymer rod. One is to incorporate side groups into the diamine moiety while the other is to attach side groups into the dianhydride moiety. Such side group incorporations are possible through only modification of diamine and dianhydride monomers with side group reactants before synthesizing PI rods, because both PMDA-PDA PI and PMDA-BZ PI are not soluble in most organic solvents and further not moldable and tractable.

So far, several *p*-phenylene diamine (PDA) derivatives with short side groups have been developed: 2,5-diamino-toluene (MEPDA), 2,5-diaminoanisole (MEOPDA), 2,5-diaminobenzotrifluoride (CF3PDA), 2,5-diaminofluorobenzene (FPDA), 2,5-diaminotetrafluorobenzene (F4PDA), 1,4-di(hydroxymethyl)-2,5-diaminobenzene (DHOMEPDA), and 1,4-di(*n*-butoxymethyl)-2,5-diaminobenzene (DBME-PDA).^{89,94-99} And, some benzidine (BZ) derivatives with short side groups are also available: 2,2'-bis(methyl)benzidine (MEBZ), 2,2'-bis(methoxy)benzidine (MEBZ), 2,2'-bis(fluoro) benzidine (FBZ), 2,2'-bis(trifluoromethyl)benzidine (CF3BZ), 3,3'-hydroxy-4,4'-diaminobiphenyl (HAB), and *o*-tolidine (TDI).^{90,92,95,135}

On the other hand, several research groups^{91,93,100-103} have attempted to incorporate short side groups into pyromellitic dianhydride (PMDA). As results of their efforts, some PMDA derivatives are available from only those research groups: 3,6-dimethyloxypyromellitic dianhydride (DMEOPMDA), 1-trifluoromethyl-2,3,5,6-benzenetetracarboxylic dianhydride (CF3DAN), and 1,4-bis(trifluoromethyl)-2,3,5,6-benzenetetracarboxylic dianhydride (DCF3DAN).^{91,93,100-103}

From these PMDA, PDA, and BZ derivatives, various PI rods can be synthesized as follows. Fully aromatic PI rods are inherently insoluble in common organic solvents, so that their soluble PAA precursors are first made by conventional synthetic process. That is, a purified dianhydride monomer is slowly added to a purified diamine monomer of equivalent mole in dry NMP and followed by stirring for 2 days to make the polymerization mixture homogeneous completely. The obtained PAA precursor solution is filtered and then cast as thin films, finally converted to the corresponding PI films by thermal imidization.

In the same manner, two different series of PI rods were synthesized: i) PMDA-PDA PI analogs - PMDA-PDA PI, PMDA-MEPDA PI, PMDA-CF3PDA PI, PMDA-MEOPDA PI, PMDA-F4PDA PI, PMDA-DHOMEPDA PI, PMDA-DBMEPDA PI, CF3DAN-PDA PI, DCF3DAN-PDA PI, and DMEOPMDA-PDA;^{91,93,100-103} ii) PMDA-BZ PI analogs - PMDA-BZ PI, PMDA-MEOBZ PI, PMDA-MEBZ PI, PMDA-FBZ, PMDA-CF3BZ PI, CF3DAN-BZ PI, CF3DAN- CF3BZ PI, and DCF3DAN-CF3BZ PI.^{90-96,100-135} Here, all thermal imidizations were conducted under nitrogen gas flow by a three-step protocol: 150 °C/30 min, 230 °C/30 min, and 380 °C/60 min with a ramping rate of 2.0 °C/min per each step.

The second approach, namely insertion of kink and bent linkages, has some freedom in selecting chemical linkage to incorporate into PI rod backbone. Adopting this approach, PMDA, PDA and BZ monomers all can be modified. To retain advantageous properties of PI rod, in practice there is, however, big limitation for such selection. Thus, the modification of either the dianhydride monomer or the diamine monomers would be better than modifying both the dianhydride and the diamines in order to minimize any degradation in the advantageous properties of PI rod. Some dianhydrides can be considered as a modified PMDA monomer, which include biphenyltetracarboxylic dianhydride (BPDA), 4,4'oxydiphthalic anhydride (ODPA), 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA), and 4,4'-hexafluoroisopropylidenediphthalic anhydride (6F). These monomers are available commercially.

From these dianhydrides a series of PAA precursors were synthesized by polycondensations with PDA monomer in the same manner as described in the previous section. Then, PAA solutions were cast and dried, finally imidized under nitrogen flow by a three-step protocol (i.e., 150 °C/30 min, 230 °C/30 min, 300 °C/30 min and 400 °C/1.5 h with a ramping rate of 2.0 °C/min):⁶ PMDA-PDA PI, BPDA-PDA PI, ODPA-PDA PI, BTDA-PDA PI, and 6F-PDA PI.

Mechanical properties of PMDA-PDA PI Derivatives in films, which were measured at room temperature by stressstrain analysis, are summarized in Table I.^{6,89,95} Young's modulus, which is the parameter of mechanical hardness, is highest for PMDA-PDA PI exhibiting the largest coherence length with irregular chain ordering. Such high modulus is reduced by incorporating short side groups into the polymer backbone: The modulus decreases in the order PMDA-PDA PI > PMDA-MEPDA PI > PMDA-MEOPDA PI > PMDA-CF3PDA PI. These moduli are correlated directly to the molecular packing coefficients. Overall, higher modulus is

 Table I. Mechanical Properties of PMDA-PDA PIs Containing

 Short Side Groups

PI Film ^a	Young's Modulus (GPa)	Stress at Break (MPa)	Strain at Break (%)
PMDA-PDA	12.2	-	-
PMDA-MEPDA	$11.4 (1.0)^{b}$	262 (26)	3.9 (0.8)
PMDA-MEOPDA	11.2 (0.3)	197 (12)	2.2 (0.6)
PMDA-CF3PDA	10.1 (1.5)	223 (10)	3.1 (0.4)

^aFilm thickness: 10-11.5 µm.

^bThe numbers in parentheses indicate 1 standard deviation.

originated from higher packing of polymer chains.^{89,95,104,134} However, the reduction of modulus due to such side groups is relatively small. This means that the high modulus nature, which is the most advantageous property of PMDA-PDA PI rod, can be retained without large sacrifice through the incorporation of such short side groups.

PMDA-PDA PI is very brittle. But the other PIs exhibit 197-292 MPa stress at break and 2.2-3.9% strain at break, depending on the side groups. In particular, the measured strains, which are an indicator of chain flexibility and toughness, are lower than the expected values. In general, both stress and strain at break are very sensitive to the quality of specimens including length-to-width ratio and defect levels in the specimen and its edges. In the measurement, PI films were prepared in a limited size, so that the length-to-width ratio of film strips was not large enough: only 25 mm length and 2.5 mm width. And, the film strips might have lots of crack-tips on their side edges. These might lead to the relatively low strains at break. Conclusively, there is confirmed indication that the brittleness of PMDA-PDA PI rod is improved by incorporating short side groups even though the strain at break was measured relatively small.

Table II is a summary of mechanical properties of PMDA-BZ PI analogs.^{90,92} PMDA-BZ PI exhibits 11.1 GPa modulus and 4% strain at break. The modulus is slightly lower than that (ca. 12.2 GPa) of PMDA-PDA PI. However, PMDA-BZ PI is relatively less brittle than PMDA-PDA PI. Considering chemical backbone structures, PMDA-BZ PI has one more phenylene moiety per the repeat unit than PMDA-PDA PI. The additionally inserted phenylene moiety may play a key role to promote the rotational freedom of the polymer chain, consequently improving the overall chain mobility that is critical to heal the mechanical brittleness.

A similar stress-strain curve is observed for the PMDA-FBZ PI. By the incorporation of fluoro side group into the polymer backbone, the low strain at break is not improved at all. In contrast, the other PIs with relatively bulky side groups show stress-strain curves that resemble that of a kink

 Table II. Mechanical Properties of PMDA-BZ PIs Containing

 Short Side Groups

PI Film ^a	Young's Modulus (GPa)	Stress at Break (MPa)	Strain at Break (%)
PMDA-BZ	$11.1 (0.1)^{b}$	212 (13)	4 (1)
PMDA-MEOBZ	10.7 (0.1)	353 (28)	11 (1)
PMDA-MEBZ	9.9 (0.1)	345 (24)	12 (1)
PMDA-FBZ	9.2 (0.1)	200 (9)	4 (1)
PMDA-CF3BZ	7.6 (0.1)	293 (11)	21 (1)

^aFilm thickness: 9.3-14.3 μm.

^bThe numbers in parentheses indicate 1 standard deviation.

type of rigid BPDA-PDA PI that shows excellent mechanical properties. That is, the relative brittleness of PMDA-BZ PI is healed significantly by incorporating side groups bulkier than the fluoro group. The strain at break is 11-21%, depending upon the incorporated side groups. The effect of side group on the improvement of strain at break increases in the order H (hydrogen) $\approx F < CH_3 \approx OCH_3 < CF_3$.

However, the modulus is reduced by incorporating side groups. The reduction of modulus is relatively large for the PMDA-CF3BZ PI, intermediate for the PMDA-MEBZ PI and PMDA-FBZ PI, and small for the PMDA-MEOBZ PI. These moduli are also dependent directly upon the molecular packing coefficients. Higher molecular packing coefficient gives higher modulus: The modulus increases linearly with the molecular packing coefficient.

6F-PDA PI is relatively weak and soft (see Table III).⁶ The other three PDA-Based PI Derivatives show excellent mechanical modulus, tensile strength and strain at break (see Table III).⁶ However, BPDA-PDA and BTDA-PDA, which exhibited high chain ordering, reveal lower modulus than that of PMDA-PDA. ODPA-PDA exhibits slightly higher modulus than that of BTDA-PDA in spite of its slightly lower coherence length with irregular ch ain ordering. In comparison, the modulus, which is the parameter of mechanical hardness, decreases in the order PMDA-PDA PI > BPDA-PDA PI > ODPA-PDA PI > BTDA-PDA PI > 6F-PDA PI. Strain at break follows the decreasing order BPDA-PDA PI > BTDA-PDA PI ≈ ODPA-PDA PI > 6F-PDA PI > PMDA-PDA PI. From these results, it is suggested that modulus, which is a mechanical charactersitic in the film plane, might result from the chain rigidity and in-plane orientation rather than the chain ordering. Higher chain rigidity, which causes higher molecular in-plane orientation, produces higher in-plane modulus. In contrast to the modulus behavior, elongation at break is relatively large for biphenyllinked BPDA-PDA PI and carbonyl-linked BTDA-PDA PI that exhibit high chain ordering. In addition, ether-linked ODPA-PDA PI in irregular chain ordering reveals strain at break comparable to that of BTDA-PDA PI. These results indicate that both the high chain ordering and the limited chain flexibility are reflected directly to the strain at break.

Tab	ole III.	Mechanical	Properties	of PDA-Based	PIs with	Vari-
ous	Chain	Rigidities				

PI Film ^a	Young's Modulus (GPa)	Stress at Break (MPa)	Strain at Break (%)
BPDA-PDA	$10.2 (0.2)^{b}$	597 (80)	47 (10)
ODPA-PDA	8.1 (0.2)	263 (20)	18 (11)
BTDA-PDA	7.1 (0.2)	248 (13)	18 (6)
6F-PDA	3.8 (0.07)	108 (20)	6(3)

^aFilm thickness: 10.0-11.5 µm.

^bThe numbers in parentheses indicate 1 standard deviation.

High Performance Polyimides for Applications in Microelectronics and Flat Panel Displays

		Optical Properties ^b				Dielectric Properties ^c		
ГІГІШ	n_{xy}	n_z	n_{av}	Δ	\mathcal{E}_{xy}	\mathcal{E}_{z}	\mathcal{E}_{av}	$\Delta \varepsilon$
PMDA-PDA	1.823	1.582	1.743	0.241	3.323	2.503	3.038	0.820
PMDA-MEPDA	1.751	1.595	1.699	0.156	3.066	2.544	2.887	0.522
PMDA-MEOPDA	1.743	1.589	1.692	0.154	3.038	2.525	2.863	0.513
PMDA-CF3PDA	1.678	1.556	1.637	0.122	2.816	2.421	2.680	0.395

Table IV. Optical and Dielectric Properties of PMDA-PDA PIs Containing Short Side Groups

"Film thickness: 10.0-11.5 μ m. "Measured at 632.8 nm (474.08 THz)." Estimated from refractive indices using Maxwell equation ($\varepsilon = n^2$).

Overall, BPDA-PDA PI exhibits exceptionally superior mechanical properties, except for its modulus lower than that of PMDA-PDA PI.

In-plane and out-of-plane refractive indices $(n_{xy} \text{ and } n_z)$ of PMDA-PDA PI derivatives, which were measured at 632.8 nm (474.08 THz in optical frequency), are listed in Table IV.^{64,89,95,105} In comparison, n_{xy} is in the increasing order PMDA-CF3PDAPI < PMDA-MEOPDAPI < PMDA-MEPDA PI < PMDA-PDA PI, whereas n_z is also in the increasing order PMDA-CF3PDA PI < PMDA-PDA PI < PMDA-MEOPDA PI < PMDA-MEPDA PI. All PI films show n_{xy} larger than n_z , regardless of the side groups. This indicates two things as follows. First, these PIs are positively birefringent polymers. That is, the polarizability along the chain axis is higher than that normal to the chain axis. Birefringence $(\Delta = n_{xy} - nz)$ in the thin film is in the increasing order PMDA-CF3PDA PI < PMDA-MEOPDA PI < PMDA-MEPDA PI < PMDA-PDA PI. Second, all the PI chains are preferentially aligned in the film plane. These are consistent with the results observed in the X-ray diffraction study as described above.

The average refractive index $[n_{av} = (2n_{xy} + n_z)/3]$ is in the increasing order PMDA-CF3PDA PI < PMDA-MEOPDA PI < PMDA-MEOPDA PI.

These refractive indices are attributed to the polarizabilities of atoms consisting of polymer backbones and their chemical bonds. In general, higher polarizability causes higher dipole moment under electromagnetic field, providing higher refractive index. The fluorine atom exhibits a relatively low polarizability because of its high electronegativity and small volume, whereas the carbon atom presents large polarizability.^{103,136} Both oxygen and hydrogen have intermediate polarizabilities.^{103,136} When these atoms involve in the formation of chemical bonds, the polarizabilities of the chemical bonds also contribute to the refractive index. Therefore, the incorporation of low polarizable atoms, as well as low polarizable chemical bonds into the polymer chain can reduce the refractive index. PMDA-CF3PDA PI shows the lowest refractive index, which is contributed from the trifluoromethyl side group. In fact, for this polymer, the fluorine atoms contribute positively to the reduction of refractive index and, however, their chemical bonds to the carbon atom contribute negatively because of the relatively high polarizabilities caused by the large difference between the electronegativities of fluorine and carbon atom. However, from the result it is evident that in the reduction of refractive index the former contribution is higher than the latter one.

Therefore, the relatively low refractive indices of the PMDA-PDA PIs containing side groups are overall attributed to the incorporations of side groups containing fluorine, oxygen and hydrogen atoms that have relatively lower polarizabilities than that of carbon atom. In comparison, the contribution in the reduction of refractive index is high for the trifluoromethyl group, intermediate for the methoxy group and low for the methyl group. In addition, the reduction of refractive index due to the incorporation of side group is also contributed in part from an increase in the free volume of the polymer caused by the steric bulkiness of side group. That is, the side group with a steric bulkiness leads to a less efficient packing of the polymer chains, resulting in an increase of free volume in the polymer film.

Dielectric constants of the PIs can be estimated from the measured refractive indices using Maxwell's equation $(\mathcal{E}=n^2)$.¹³⁷ The results are illustrated in Table III. Here, it is noteworthy that the dielectric constants, which were obtained at the optical frequency, are attributed mainly to electronic polarization and in part to atomic polarization: The dipole orientation polarization would not contribute to the dielectric constants because of its limited slow process.¹³⁸ PMDA-PDA PI exhibits the highest in-plane and average dielectric constant (ε_{rv} and ε_{av}), whereas PMDA-MEPDA PI shows the highest out-of-plane dielectric constant (\mathcal{E}_{r}). In contrast, PMDA-CF3PDA PI exhibits the lowest ε_{xy} , ε_{z} , and ε_{ay} . In addition, this PI shows the lowest anisotropy in the dielectric constant. Large anisotropy in the dielectric constant often causes near-coupled-noise due to crosstalks in the performance of microelectronic devices.53,54 Therefore, PMDA-CF3PDA PI may be suitable for the applications in microelectronic devices because of the low dielectric constant and anisotropy.

Table V presents n_{xy} s and n_z s of PMDA-BZ PI analogs in thin films.^{90,92} These PIs also exhibit n_{xy} larger than n_z as observed in PMDA-PDA PI analogs. This indicates that all the PIs are the positively birefringent polymers in which the

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		Optical F	Properties ^b		Dielectric Properties ^c			
	n_{xy}	n_z	n_{av}	Δ	\mathcal{E}_{xy}	\mathcal{E}_{z}	\mathcal{E}_{av}	$\Delta \varepsilon$
PMDA-BZ	1.851	1.591	1.764	0.260	3.426	2.531	3.113	0.895
PMDA-MEOBZ	1.745	1.598	1.693	0.156	3.045	2.555	2.867	0.490
PMDA-MEBZ	1.753	1.579	1.695	0.174	3.071	2.492	2.872	0.579
PMDA-FBZ	1.805	1.575	1.729	0.230	3.258	2.482	2.989	0.776
PMDA-CF3BZ	1.636	1.512	1.595	0.124	2.677	2.286	2.543	0.390

Table V. Optical and Dielectric Properties of PMDA-BZ PIs Containing Short Side Groups

"Film thickness: 9.3-14.3 μ m. "Measured at 632.8 nm (474.08 THz)." Estimated from refractive indices using Maxwell equation ($\varepsilon = n^2$).

Table VI. Optical and Dielectric Properties of Films of PDA-Based PIs with Various Chain Rigidities

DI Eilm ^{a}		Optical Properties ^b				Dielectric Properties ^c			
1111111	n_{xy}	n_z	n_{av}	Δ	\mathcal{E}_{xy}	\mathcal{E}_{z}	\mathcal{E}_{av}	$\Delta \varepsilon$	
BPDA-PDA	1.8474	1.6141	1.7696	0.2333	3.413	2.605	3.132	0.808	
ODPA-PDA	1.7801	1.6371	1.7324	0.1430	3.169	2.680	3.001	0.489	
BTDA-PDA	1.7692	1.6383	1.7256	0.1309	3.130	2.684	2.978	0.446	
6F-PDA	1.5847	1.5762	1.5819	0.0112	2.511	2.484	2.502	0.027	

"Film thickness: 10.0-11.5 μ m. "Measured at 632.8 nm (i.e., 474.08 THz). "Estimated from refractive indices using Maxwell equation ($\varepsilon = n^2$).

polarization along the chain axis is higher than that normal to the chain axis. In comparison, n_{xy} is in the decreasing order PMDA-BZ PI > PMDA-FBZ PI > PMDA-MEBZ PI > PMDA-MEOBZ PI > PMDA-CF3BZ PI, whereas n_z is in the decreasing order PMDA-MEOBZ PI > PMDA-BZ PI > PMDA-MEBZ PI > PMDA-FBZ PI > PMDA-CF3BZ PI. n_{av} decreases in the order PMDA-BZ PI > PMDA-FBZ PI > PMDA-MEBZ PI > PMDA-MEOBZ PI > PMDA-CF3BZ PI. Δ is in the decreasing order PMDA-BZ PI > PMDA-FBZ PI > PMDA-MEBZ PI > PMDA-BZ PI > PMDA-FBZ PI > PMDA-MEBZ PI > PMDA-BZ PI > PMDA-FBZ PI > PMDA-MEBZ PI > PMDA-MEOBZ PI > PMDA-FBZ PI > PMDA-MEBZ PI > PMDA-FBZ PI > PMDA-FBZ PI > PMDA-FBZ PI > PMDA-MEOBZ PI > PMDA-FBZ PI > PMDA PI > PMDA PI > PMDA-FBZ PI > PMDA PI >

Overall, the incorporation of side groups on the polymer backbone lowers n_{xy} and n_z of the PMDA-BZ PI film, resulting in the decreases in both the bulk refractive index n_{av} and the optical anisotropy Δ . The effect of side group to the optical properties is rated in the increasing order H (hydrogen) $< F < CH_3 < OCH_3 < CF_3$. This result can be understood with considering chemical and structural characteristics of the side groups as discussed in the previous section. In conclusion, the refractive index of PMDA-BZ PI is reduced by the incorporation of side groups having relatively low polarizabilities and large bulkiness.

From the measured refractive indices, dielectric constants and anisotropies are also estimated and summarized in Table V. Considering dielectic constants and their anisotropy, PMDA-CF3BZ PI is a good candidate material to fabricate microelectronic devices. From the results, again it is suggested that the incorporation of short side groups having very low polarizability, such as CF₃ and other perfluorinated short alkyls, into a rodlike polymer backbone is one of the most useful routes to make high preformance polyimides which can exhibit isotropically low refractive index and dielectric constant.

As listed in Table VI, all the PDA-Based PI Derivative films also show n_{xy} larger than n_z , resulting in an optical anisotropy.⁶ Δ is 0.2333 for BPDA-PDA PI, 0.1430 for ODPA-PDA PI, 0.1309 for BTDA-PDA PI, and 0.0112 for 6F-PDA PI. PMDA-PDA PI with the highest chain rigidity exhibits the largest optical anisotropy, whereas 6F-PDA PI, which is structureless with the lowest rigidity, reveals the lowest optical anisotropy. The others exhibit intermediate optical anisotropies. These anisotropies result from the inplane orientation of polymer chains in which the principal polarization is along the chain axis. This is directly correlated to the molecular in-plane orientation detected on the X-ray diffraction patterns.

Dielectric constants, which are estimated from the refractive indices, are summarized in Table VI.⁶ Depending on the backbone structures, ε_{xy} varies over 2.511-3.413 while ε_z changes over 2.484-2.684. ε_{av} is in the range of 2.502 -3.132. $\Delta \varepsilon$ is 0.822 for PMDA-PDA PI, 0.808 for BPDA-PDA PI, 0.489 for ODPA-PDA PI, 0.446 for BTDA-PDA PI, and 0.027 for 6F-PDA PI.

In comparison, both n_{xy} and ε_{xy} follow the decreasing order BPDA-PDA PI > PMDA-PDA PI > ODPA-PDA PI > BTDA-PDA PI > 6F-PDA PI, respectively, whereas the n_z and ε_z are in the decreasing order BTDA-PDA PI > ODPA-PDA PI > BPDA-PDA PI > PMDA-PDA PI > 6F-PDA PI, respectively. In addition, the n_{av} and ε_{av} are in the decreasing order BPDA-PDA PI > PMDA-PDA PI > ODPA-PDA PI > BTDA-PDA PI > 6F-PDA PI, respectively.

Just counting dielectric properties, 6F-PDA PI is suitable for the applications in the microelectronic devices, owing to its relatively low refractive index and dielectric constant with almost negligible anisotropy.

As described above, the dielectric constant of a PI can be reduced by incorporating atoms and/or groups having lower polarizabilities and further reduced by increasing free molecular voids due to the incorporation of side groups. However, these approaches have limits in reducing the dielectric constants of PIs; the lower limit in the dielectric constants of PIs is known to be around 2.7. The lowest dielectric constant achievable from organic polymers is around 2.0, which has been obtained from polytetrafluoroethylene (namely, Teflon[™]).

An alternative approach to significantly reduce the dielectric constants of PIs is the incorporation of nanoscale pores (namely, nanoscale voids) into the PIs; air (or vacuum) owns the lowest dielectric constant, 1.0, thus incorporating larger amount of air nanpores into PIs can deliver larger reduction in the dielectric constant. So far two approaches on how to incorporate nanopores in PIs have been introduced.¹³¹ One approach is incorporating hollow silica spheres into a PI,⁹¹ while another approach is generating nanopores by preparing block copolymers with the majority phase comprising polyimide and the minor phase consisting of a thermally labile block where the two dissimilar blocks are phase-seprated in nanoscale and the labile blocks are selectively removed via thermal treatments, leaving pores.92,93 However, the major drawback of the second approach is the collapse of the nanopores during thermal cycles in a post fabrication process after the nanopores were generated in the first thermal treatment; the nanoporous PIs with the collapsed pores exhibits no longer low dielectric constant. Conclusively, the first approach, incorporating thermally, dimensionally stable hollow nanospheres is the most realistical approach to deliver low and ultralow dielectric constant PI materials.

Light-Emitting PIs

The development of organic and polymeric materials for use in the fabrication of light-emitting devices (LEDs) has been directed toward finding ways to improve light-emitting performance and reliability, as well as to control the wavelength and band width.^{139,140} However, one of the major problems in the application of such materials to LEDs is their degradation under continuous operation, which is caused by Joule heating.¹⁴¹ The shortcomings of these materials may be overcome by the incorporation of light-emitting moieties into an aromatic polymer backbone, such as those of PIs. This approach has been adopted by several research groups in recent attempts to synthesize light-emitting polyetherimides and polyimides.^{83-88,139-145} Mal'tsev *et al.*^{141,142} have synthesized



Figure 11. Chemical structure of the synthesized light-emitting polyimides.

polyetherimides containing 9,10-bis(phenylthio)anthracene units which emit blue-green light in the range 420-700 nm. Kakimoto and coworkers¹⁴³ have reported a series of polyimides synthesized from 2,5-bis(4-aminostyryl)pyrazine, a light-emitting diamine monomer derived from 2,5-distyrylpyrazine. These polymers emit orange-red light with an emission maximum at around 560 nm (= λ_{max}). It was found that the value of λ_{max} is independent of the number of dianhydride units, but the emission intensity is strongly dependent on the number of these units. Recently there have been reported two new π -conjugated diamines, 5,5'-bis(4-aminophenyl)-2,2'-bifuryl (PFDA) and 2,2'-bis(furyl)benzidine (FurylBZ), and their PIs, prepared from pyromellitic dianhydride (PMDA) (Figure 11).^{83-88,146-149} These monomers and their polymers strongly emit blue light.

The usages of the PDFA and FurylBZ emitters were extended for the synthesis of PIs of other aromatic dianhydrides such as ODPA and 6F, yielding the polyimides ODPA-PFDA PI, 6F-PFDA PI, ODPA-FurylBZ PI, and 6F-FurylBZ PI (Figure 11).⁸⁵ The UV-visible absorption and light-emitting characteristics of the resulting PI films were investigated, and the quantum efficiency in the light emission was determined.⁸⁵ In addition, the structure, thermal stability, refractive index and dieletric constant of the polymer films were determined.⁸⁵

Figure 12(a) shows the UV-visible absorption and PL spectra of the ODPA-PFDA PI and 6F-PFDA PI films, which are compared with the spectra of PFDA in dioxane and PMDA-PFDA PI in film form. The PI films exhibit broad featureless absorptions for wavelengths less than 520 nm. In general, the chromophoric aromatic imide rings of conventional aromatic polyimides cause them to absorb at wavelengths less than 470 nm. This absorption overlaps with that





Figure 12. (a) UV-visible absorption (Abs) and photoluminescence (PL) spectra of PFDA (1.5×10^{-5} g/mL in 1,4-dioxane) and of polyimides in thin films; PFDA was excited at 340 nm, whereas the polyimides were excited at 380 nm. (b) UV-visible absorption (Abs) and photoluminescence (PL) spectra of FurylBZ (1.5×10^{-5} g/mL in 1,4-dioxane) and of polyimides in thin films; FurylBZ was excited at 340 nm, whereas the polyimides were excited at 340 nm, whereas the polyimides in thin films; FurylBZ was excited at 340 nm, whereas the polyimides were excited at 340 nm, whereas the polyimides were excited at 340 nm, whereas the polyimides in thin films; FurylBZ was excited at 340 nm, whereas the polyimides were excited at 380 nm.

of the PFDA unit, causing the PI films to exhibit a broader absorption spectrum than pure PFDA. The optical band gap of PFDA, which corresponds to the π - π * transition of the conjugated system, is estimated to be 2.96 eV by extrapolation of the absorption spectrum to long wavelengths. This band gap is larger than that of PPV (2.5-2.6 eV).¹⁵⁰

The polyimides in the films emit the strongest PL spectra when excited at 380 nm. Both ODPA-PFDA PI and 6F-PFDA PI exhibit single emission peaks rather than multiple peaks, in contrast to PMDA-PFDA PI which has a PL spectrum very similar to that of PFDA. The emission peak is centered at 480 nm (blue-green light) for ODPA-PFDA PI and at 460 nm (blue light) for 6F-PFDA PI. These emission peaks are red-shifted compared to those of PFDA and PMDA-PFDA PI. This shift may be due in part to the electron affinities of the ODPA and 6F units, which influence the π - π * transition of PFDA units on the polymer backbone, and also to the dilution of the light-emitting PFDA unit by ODPA and 6F units. In addition, the full-width at half maximum (*FWHM*) of the emission peaks of ODPA-PFDA PI and 6F-PFDA PI are estimated to be 26 and 23 nm, respectively. These emission peaks are much narrower than those of PFDA and PMDA-PFDA PI (56 and 63 nm *FWHM*, respectively). It is noteworthy that ODPA-PFDA PI and 6F- PFDA PI exhibit narrower PL spectra than any other lightemitting polymer studied to date.

Figure 12(b) shows the UV-visible absorption and PL spectra of the films of ODPA-FurylBZ PI and 6F-FurylBZ PI, which are compared to those of FurylBZ in dioxane and PMDA-FyrylBZ PI in film form. The PI films show broad absorptions at wavelengths less than 400 nm in comparison to the absorption of FurylBZ monomer. FurylBZ has an optical band gap of 3.42 eV, which corresponds to the π - π^* transition of the conjugated system. This value is much larger than the band gaps of its structural isomer PFDA and PPV. The following two factors are possible causes of the large band gap of FurylBZ. First, it is possible that the π -conjugation forms only along the kinked structure composed of the benzidine main unit and the two furyl side groups. This kinked π -conjugated structure would have a relatively large band in the π - π^* transition. Second, in order to minimize steric hinderance the ring components of FurylBZ are not copolanar. In comparison to the absorption of FurylBZ monomer, its PI films show broad absorptions at wavelength less than 400 nm. Here, the band gaps of the PIs would not be estimated because the measured band gaps are not those of the pure FurylBZ, but also contain contributions due to the chromophoric aromatic imide rings, as mentioned above for the case of PFDA-based PIs.

The FurylBZ-based PIs in films also emit the strongest PL spectra when excited at 380 nm. For both ODPA-FurylBZ PI and 6F-FurylBZ PI, the PL spectra exhibit single emission peaks rather than multiple peaks, which is similar to the behavior of FurylBZ but different from that of PMDA-FurylBZ PI. ODPA-FurylBZ PI gives an emission peak centered at 530 nm (green light) and 6F-FurylBZ PI gives a peak centered at 525 nm (green light). The emission peaks of these PIs are highly red-shifted compared to those of the FurylBZ and PMDA-FurylBZ PI. This shift may be due in part to the electron affinities of the ODPA and 6F units, which influence the π - π^* transition of the FurylBZ units on the polymer backbone, and to the dilution of the light-emitting FurylBZ unit by ODPA and 6F units, as mentioned above in relation to the photoluminescent characteristics of the PFDA-based PIs. In the emission spectra, ODPA-FuryIBZ PI has a peak width of 121 nm FWHM, whereas 6F-FurylBZ PI has a width of 74 nm FWHM. These emission peaks are broader than those of FurylBZ and PMDA-FurylBZ PI (73 and 64 nm FWHM, respectively), and is also broader than those of the PFDA-based PIs. Although the PL spectra of the FurylBZ-based PIs are broader than those of the PFDA-based PIs, they are still narrower than those of all other light-emitting polymers reported in the literature.

In addition, PL quantum yield Φ_f measurements were conducted for all PIs in films. The OPDA-PFDA PI and 6F-PFDA PI films have high quantum yields ($\Phi_f = 7.3\%$ and 14.9%, respectively) compared to the quantum yield of the PMDA-PFDA PI film ($\Phi_f = 1.2\%$). In particular, the Φ_f value of 6F-PFDA PI is larger than that of poly(2-methoxy-5-(2'ethyl)hexyloxy-*p*-phenylenevinylene) ($\Phi_f = 8.5 \cdot 11.5\%$),¹⁵¹ which emits orange light. On the other hand, the OPDA-FurylBZ PI and 6F-FurylBZ PI films have yields of $\Phi_f =$ 7.6% and 8.3%, respectively. These values are slightly higher than the value for the PMDA-FurylBZ PI film ($\Phi_f = 7.4\%$).

In comparison to the quantum yields of PFDA ($\Phi_f = 92.0\%$) and FurylBZ in 1,4-dioxane ($\Phi_f = 52.0\%$), the PI films show relatively low quantum yields. This might be due to the morphological structures formed in the PI films. X-ray diffraction analyses were performed to elucidate the morphological structures in the films, and the X-ray diffraction patterns obtained are compared in Figure 13. For the PMDA-PFDA PI film, well-resolved multiple (00l) peaks, as well as some (hkl) peaks, are detected in the transmission pattern, whereas only (hkl) peaks are observed in the reflection pattern. These patterns indicate that parts of the PI film are structurally ordered, and that the polymer chains are highly aligned in the film plane. One can obtain some structural information from these X-ray patterns, although the full crystal structure is not yet determined. The diffraction peak at 4.11° (2 θ) (21.5 Å d-spacing), which corresponds to the (001) diffraction, is estimated from the Scherrer relation to have a very high coherence length of 168 Å.⁶ The (hkl) diffractions in the reflection pattern have a coherence length of about 42 Å (36-48 Å). It is therefore concluded that this PI film contains structurally ordered phases with a dimension of approximately $168 \times 42 \times 42$ Å. The overall crystallinity is estimated to be 26% from the reflection pattern, and 36% from the transmission pattern. Structural ordering is also observed in the ODPA-PFDA PI film. However, a low coherence length of less than 52 Å is obtained for all of the diffraction peaks, and the overall crystallinity in the film is estimated to be only 13-15% from the reflection and transmission patterns.

In contrast, the 6F-PFDA PI film is almost amorphous. Only a weak diffraction indicating short-range ordering is detected at 5.58°. The coherence length of this diffraction is only 37 Å, which is slightly larger than the length of just one repeat unit in the backbone. The mean interchain distance is estimated to be 5.8-5.9 Å, which is larger than the interchain distances of the other two PIs (4.2-4.5 Å). Similar featureless X-ray patterns are observed for all of the FurylBZ-based PI films (see Figure 13).

In conclusion, it is found that a higher degree of structural ordering gives a lower quantum yield. This behavior may be linked to charge transfer between the dianhydride unit and diamine unit in the PIs, which in general are electronically deficient and rich, respectively. Both intra- and inter-mole-cular charge-transfer (CT) interactions between dianhydride and diamine units are known to be favorable when the polymer undergoes structural ordering.^{106,152-154} Thus, the low quantum yield in the highly ordered PMDA-PFDA PI might be due to a large amount of energy transfer from the excited

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Figure 13. Wide angle X-ray diffraction patterns of PFDA- and FurylBZ-based PIs in thin films: Refl, reflection pattern; Trans, transmission pattern. A CuK_{α} radiation source was employed.

PFDA units in the polymer backbone to the CT sites, which give a weak emission. In contrast, this CT interaction is relatively weak in the ODPA-PFDA PI and 6F-PFDA PI films, as well as the FurylBZ-based PI films, which are less ordered. In addition, the relatively large size of the ODPA, 6F, and FurylBZ units in the polymer backbone dilute the light-emitting units in the film specimen. These morphological features may contribute positively to the emission of the PFDA and FurylBZ units in the backbone, enhancing the quantum yield.

In addition, tests on the thermal stability of the PIs showed them to be stable up to 370-396 °C, depending on polymer type. The stability of these polymers is due to the stable phenyl, imide and furyl constituents in the polymer backbone.

PIs for Liquid Crystal Alignment

Nonphotoreactive PIs. One of the most recently developed and important applications of PIs is their use in liquid crystal (LC) alignment layers for LC flat-panel display devices.¹⁵⁵⁻¹⁵⁹ PIs are widely used as LC alignment layers

because of their advantageous properties, such as excellent optical transparency, adhesion, heat resistance, dimensional stability and insulation.^{65-73,95,124,125,155,156,160-167} Such PI film surfaces need to be treated if they are to produce a uniform alignment of LC molecules with a defined range of pretilt angle values.^{37-42,55,83,84,108-122} At present, a rubbing process using a velvet fabric is the only technique adopted in the LC display industry to treat PI film surfaces for the mass-production of flat-panel LC display devices. This process has become the method of choice because of its simplicity and the controllability with this method of both the LC anchoring energy and the pretilt angle.^{65-73,95,124,125,155-171} Much effort has been exerted to understand the mechanism behind the alignment of LC molecules on the rubbed polymer surface. A variety of factors have been proposed to explain the surface anchoring and alignment mechanism of the LC molecules: (i) microgrooves in connection with anisotropic LC orientational elasticity via steric interaction,¹⁷²⁻¹⁷⁸(ii) polymer molecules from the velvet fabric deposited and oriented on the alignment layer surface during the rubbing process, 179,180 (iii) surface electric fields,¹⁸¹ (iv) anisotropically oriented polymer chains, 65-73,95,124,125,155-171 (v) a near-surface order parameter different from the bulk LC molecules,^{182,183} and (vi) coupling of a bending mode of the LC director to the surface electric fields (i.e., flexoelectricity).¹⁸⁴ Of these suggestions, the two models for the alignment process that have received the most attention are the microgroove mechanism¹²³⁻¹²⁹ and the anisotropic polymer chain orientation mechanism,^{65-73,95,124,125,155-171} although the exact mechanism of LC alignment is still a subject of debate.

In addition to the uniform, unidirectional alignment of LC molecules, their pretilt angle (i.e., their out-of-plane tilt angle) plays the most important role^{155,156} in determining the optical and electrical performance of the industrial LC display devices that currently use nematic LC molecules. Much effort has also been expended to achieve the desired LC pretilt angle and to understand the mechanism behind LC pretilt phenomena. Some investigators have proposed that the outof-plane LC tilt angle is governed by van der Waals interactions between the LC molecules and the alkyl side chains of the polyimide.^{65-73,95,124,125,155-171,185} In contrast, other investigators have suggested that LC pretilt is determined by the polymer backbone structure but is independent of the length of the side chains.¹⁸⁶⁻¹⁸⁹ The exact mechanism controlling the LC pretilt angle on rubbed surfaces has not yet been unambiguously elucidated.

For the study of LC alignment mechanism, it was chosen a series of poly{*p*-phenylene 3,6-bis[4-(*n*-alkyloxy)phenyloxy] pyromellitimide} (Cn-PMDA-PDA PI) from various PMDA-based PIs because of its easily controlled structural features; it is a well-defined brush polymer composed of aromatic-aliphatic bristles set into a fully rod-like polymer backbone (two bristles per chemical repeat unit of the polymer backbone) (Figure 14).^{65-68,190,191} To better understand the mechanism of LC alignment by the Cn-PMDA-PDA PI surfaces, there were measured the surface orientational distributions of both the main chains and of the bristles (i.e., side groups) of the PI film before and after rubbing, using optical phase retardation analysis and linearly polarized FTIR spectroscopy.^{65-68,190,191}

To obtain information about the orientation of polymer chains produced by the rubbing process, PI films were rubbed and their optical phase retardation measured. Figure 15 displays polar diagrams of the optical phase retardation with respect to the angle of rotation of PI films rubbed with a rubbing density of 120. As seen in Figure 15, all rubbed PI films exhibit a maximum retardation along the direction $180^{\circ} \leftrightarrow 0^{\circ}$, which is parallel to the rubbing direction, but a minimum retardation along the direction $90^{\circ} \leftrightarrow 270^{\circ}$, which is perpendicular to the rubbing direction. All PI chains were determined to be positively birefringent along the rubbing direction by spectroscopic ellipsometry. Taking this fact into account, the polar diagram results confirm that for all rubbed films, the main director of the PI chains after orientation by rubbing is parallel to the rubbing direction. In contrast, the polar diagram of the optical phase retardation of an unrubbed



Figure 14. Chemical structures of fully rodlike poly(*p*-phenylene pyromellitimide)s with 4-(*n*-alkyloxy)phenyloxy bristles (Cn-PMDA-PDA PIs).



Figure 15. Polar diagrams of the variation of the retardation with the angle of rotation of the film in optical phase retardation measurements of Cn-PMDA-PDA PI films rubbed with a rubbing density of 120: (a) C4-PMDA-PDA PI; (b) C6-PMDA-PDA PI; (c) C7-PMDA-PDA PI; (d) C8-PMDA-PDA PI.

PI film (data not shown) is isotropic with respect to the angle of rotation of the film, confirming that the polymer chains of unrubbed films lie randomly in the film plane. C4-PMDA-PDA

C6-PMDA-PDA

C7-PMDA-PDA

C8-PMDA-PDA

250

300

Figure 16. Variations of the in-plane birefringence with rubbing density of rubbed Cn-PMDA-PDA PI films.

150

Rubbing density

200

100

50

0.006

0.005

0.004

0.003

0.002

0.001

0.000

(

Birefringence Δ_{XV}

Figure 16 shows the variation of the in-plane birefringence Δ_{xy} with rubbing density for the PI films, which is produced by the rubbing process. For all PI films, the Δ_{xy} rapidly increases with rubbing density up to a rubbing density of 50 (for C4-PMDA-PDA, C6-PMDA-PDA, C7-PMDA-PDA PI) or 100 (for C8-PMDA-PDA PI) and then more slowly increases with further increases in the rubbing density, finally leveling off above a rubbing density of 300. These results confirm that the polymer chains in the surfaces of the PI films are oriented along the rubbing direction by the rubbing process, and that preferential orientation can be achieved by rubbing at a rubbing density greater than 50 (for C4-PMDA-PDA, C6-PMDA-PDA, C7-PMDA-PDA PI) or 100 (for C8-PMDA-PDA PI).

Figure 17 presents two representative IR spectra of a C6-PMDA-PDA PI film rubbed at a rubbing density of 120, one measured with the IR light polarized parallel to the rubbing direction, the other measured with the IR light polarized perpendicular to the rubbing direction. In both these FTIR spectroscopic measurements, only modes with in-plane components are detected because only normal incidence spectra were measured. The vibrational modes were assigned with the aid of results previously reported for other PIs.^{10-12,107-110,122-125,169} The bands at 1780, 1733, 1515, and 1364 cm⁻¹ are due to the symmetric and asymmetric C=O stretching vibrations of the imide ring, the C=C stretching vibration of the PDA unit, and the C-N stretching vibration of the imide bond respectively, all of which are associated with the polymer main chain structure. The band at 1505 cm⁻¹ is due to the C=C stretching vibration of the phenyloxy unit in the side chain. Further, the asymmetric and symmetric CH₂ stretching vibrational modes are detected at 2923 and 2852 cm⁻¹ respectively. The IR spectra of the rubbed film differ depending on whether the IR light is polarized parallel or perpendicular to the rubbing direction, indicating that the rubbed PI film is anisotropic in the film



Figure 17. FTIR dichroic spectrum of a C6-PMDA-PDA PI film rubbed with a rubbing density of 120. The solid and dashed lines are the FTIR spectra with the IR light polarized parallel to the rubbing direction and with the IR light polarized parallel perpendicular to the rubbing direction respectively.

plane. Similar dichroic IR spectra were observed for the rubbed films of the other PIs (spectra not shown). In contrast, the unrubbed PI film reveals no IR dichroism dependence (spectra not shown).

IR spectroscopic measurements using a linearly polarized IR light source were further carried out on the rubbed PI film as a function of the angle of rotation of the film. The variations of the peak intensities of selected IR bands with the angle of rotation of the film are plotted in Figure 18 as polar diagrams. As shown in Figure 18(a) and (b), the imide C-N band at 1364 cm⁻¹ and the C=C band of the PDA unit at 1515 cm⁻¹ are more intense when the incident beam is polarized parallel to the rubbing direction. Both the imide C-N bond and the PDA unit are parts of the polymer backbone, and lie along the polymer main chain axis. The anisotropic polar diagrams of the IR bands corresponding to these moieties indicate that rubbing causes these moieties, and therefore the main axes of the polymer chains, to be oriented along the rubbing direction.

In contrast, as shown in Figure 18(c) the intensity of the asymmetric C=O vibration of the imide ring at 1733 cm⁻¹ is enhanced when the polarization of the IR beam lies along the direction $250^{\circ} \leftrightarrow 70^{\circ}$, which is at an angle of 70° with respect to the rubbing direction, indicating that the imide C=O bond is oriented by rubbing in this direction. This conclusion is consistent with the chemical structure shown in Figure 14 and with the orientation of the imide C=O vibration of the phenyloxy unit at 1505 cm⁻¹ shows that the intensity of this mode is enhanced when the beam polarization is perpendicular to the rubbing direction (see Figure 18(d)). This suggests that the long axis of the phenyloxy unit in the bristle becomes aligned by the rubbing process in a direction perpendicular to the polymer main chain axis.



Figure 18. Polar diagrams of the intensities of some specific vibrational peaks of a C6-PMDA-PDA PI film rubbed with a rubbing density of 120, measured with linearly polarized IR spectroscopy as a function of the angle of rotation of the film: (a) v (N-C) at 1364 cm⁻¹; (b) v(C=C_{PDA}) at 1515 cm⁻¹; (c) v_{as} (C=O) at 1733 cm⁻¹; (d) v(C=C_{Phenyloxy}) at 1505 cm⁻¹; (e) v_{as} (CH₂) at 2923 cm⁻¹; (f) v_s (CH₂) at 2852 cm⁻¹.

Figure 18(e) and (f) show the polar diagrams for the CH_2 asymmetric and symmetric stretching vibrations, which produce peaks at 2923 and 2852 cm⁻¹ respectively. The intensities of both these modes are enhanced when the beam polarization is perpendicular to the rubbing direction. Given that the CH_2 asymmetric and symmetric stretching vibrations possess dipole moment vectors perpendicular to the alkyl chain axis, it is concluded that the *n*-hexyl end group of the bristle is oriented parallel to the rubbing direction by the rubbing process.

IR spectroscopic measurements using linearly polarized IR light as a function of the angle of rotation of the film were also carried out for rubbed films of the other PIs, yielding results similar to those described above for the rubbed C6-PMDA-PDA film.

The IR results collectively indicate that, for all of the PI films studied, rubbing the film surface causes orientation of the polymers into an arrangement in which the polymer main chains and the *n*-alkyl bristle end groups are oriented parallel to the rubbing direction and the phenyloxy bristle units are oriented perpendicular to the rubbing direction.

In the light of the above findings on the polymer segmental orientations, it is worth devoting further attention to the Δ_{xy}

variations of the PI films with rubbing density shown in Figure 16. As seen in the figure, the Δ_{xy} value at a given rubbing density over the rubbing density range of 0-300 always increases in the order C4-PMDA-PDA PI < C6-PMDA-PDA PI < C7-PMDA-PDA PI < C8-PMDA-PDA PI. Several factors could potentially contribute to this trend. First, consider the contribution to the Δ_{xy} value of the polymer segmental orientations in the rubbed PI films. All the PIs have the same basic chemical structure (a PMDA-PDA backbone, a phenyloxy bristle unit, and an *n*-alkyl bristle end group), but with different lengths of the *n*-alkyl bristle end group (see Figure 14). Moreover, as described above, the main director of each polymer segment oriented by the rubbing process is the same for all the PIs. These facts suggest that the contribution of the parallel oriented polymer backbone and of the perpendicular oriented phenyloxy bristle unit to the Δ_{xy} value should be the same for all PI films rubbed at a given rubbing density. However, the contribution of the parallel oriented *n*-alkyl end group in the bristle to the Δ_{xy} value will depend on its length, with longer *n*-alkyl end groups contributing more positively to the Δ_{xy} value. Second, consider the degree of overall polymer chain orientation in the PI films rubbed at a given rubbing density. The deformation response characteristics of PI films to the shear force caused by contact with the fibers during the rubbing process are related to the film ductility, which is in turn associated with the length of the *n*-alkyl end group of the bristle. As a result, the degree of overall polymer orientation in PI films rubbed at the same rubbing densities will vary across the series of PIs tested in the present study. Therefore, the different Δ_{vv} values in the PI films rubbed at a given rubbing density are attributed to differences in the contributions of the *n*-alkyl end group orientations as well as to differences in the degree of overall polymer chain orientation in the rubbed films.

As described above, at the surfaces of all of the rubbed Cn-PMDA-PDA PI films, the polymer main chains and the *n*-alkyl bristle end groups were oriented along the rubbing direction, whereas the phenyloxy bristle units were oriented perpendicular to the rubbing direction. The rubbed film surfaces of C4-, C6-, and C7-PMDA-PDA PI were found to induce LC alignment perpendicular to the rubbing direction. The anchoring energies of these perpendicular LC alignments were very large, with values comparable to those observed for conventional PI alignment layers, which induce LC alignment parallel to the rubbing direction. The unusual tendency of LC molecules with large anchoring energies to align perpendicular to the rubbing direction is driven by the favorable anisotropic interactions of LC molecules with the perpendicularly oriented phenyloxy bristle units, which override the interactions of the LC molecules with the polymer main chains, the *n*-alkyl bristle end groups, and the grooves in the film surface. However, rubbed surfaces of the C8-PMDA-PDA PI film induced LC alignment parallel to the rubbing direction, even though this PI has only one to four more carbons in the *n*-alkyl bristle end group in comparison to the other PIs.

Taken together, the LC alignment, surface morphology, and polymer segmental orientation results indicate that the *n*-alkyl bristle end groups play an important role in LC alignment on rubbed Cn-PMDA-PDA PI films, and that this role is dependent on the length of the *n*-alkyl chain; specifically, the *n*-alkyl bristle end groups oriented parallel to the rubbing direction hinder perpendicular LC alignment because of their van der Waals interactions with the aliphatic tails of the LC molecules. The critical length of the *n*-alkyl bristle end group at which the LC alignment at the rubbed PI films changes from perpendicular to parallel is eight carbons (i.e., the *n*-octyl end group). In conclusion, LC alignment on the surfaces of rubbed PI films is determined by a play-off between the directionally anisotropic interactions of LC molecules with (i) the oriented segments of the polymer main chains, (ii) the oriented segments of the bristles, and (iii) the microgrooves.

Photoreactive PIs. As discussed in the above section, PI films are widely used as LC alignment layers in LC flat-panel display devices because of their advantageous properties such as excellent optical transparency, adhesion, heat resistance, dimensional stability, and insulation. Such PI film surfaces need to be treated if they are to produce a uniform alignment of LC molecules with suitable pretilt angles. At present, a rubbing process using velvet fabrics is the only technique adopted in the LC display industry for the treatment of PI film surfaces in the mass-production of flat-panel LC display devices. This process has become the method of choice because it is simple and enables the control of LC alignment. However, the process has some shortcomings, such as dust generation, electrostatic problems, and poor control of rubbing strength and uniformity. The search for new methods that do not suffer from the shortcomings of the rubbing process has led to the development of several approaches to polymer alignment layer surface treatment based on irradiation of the polymer with linearly polarized ultraviolet light (LPUVL).41,48,49,74-82,192-210 These techniques have attracted considerable attention in academia and industry because they offer the possibility of rubbing-free production of LC aligning films.

A representative photoalignment material is poly(vinyl cinnamate) (PVCi).¹⁹⁷⁻¹⁹⁹ In fact, this polymer was introduced in 1959 as a negative photoresist.²¹¹ The cinnamate side groups in the polymer are known to undergo [2+2] photo-dimerzation by UV light exposure.²¹¹ The photodimerization generates cross-links in the polymer via cyclobutane ring formation, leading to the insolubilization of the polymer.²¹¹ The PVCi and its derivatives in thin films were reported to have an ability to align LC molecules in the direction perpendicular to the polarization axis of the linearly polarized UV light when they were exposed to the linearly polarized

UV light.¹⁹⁷⁻²¹⁰ For this phenomenon, controversial debates have been made so far as follows. Schadt and coworkers¹⁹⁷⁻¹⁹⁹ have proposed a photoalignment mechanism that the polymer chains are oriented by the photodimerization of cinnamate side groups in the polymer film, and the oriented polymer chains induce LC molecules to align along the axis of the oriented polymer chains at the surface. Instead, Ichimura and coworkers²⁰² have suggested a different photoalignment mechanism. That is, the cinnamate groups in the polymer film undergo simultaneously photodimerization and photoisomerization in part. The photoisomerized cinnamate groups induce the alignment of LC molecules while the photodimerized polymers enhance the thermal stability of the LC alignment. Conclusively, the photoalignment mechanisms of these polymers have not yet been understood fully. Moreover, these polymers have low T_g , so even though the polymer chains in the film are oriented preferentially by exposure to LPUVL, they remain mobile after treatment and their chain orientation is not stable with respect to environmental influences such as temperature change. In addition, these polymer films are known to have a weak anchoring energy for LCs, resulting in severe reliability problems for LC devices fabricated from these polymers.²⁰⁵⁻²¹⁰ Thus there remain significant obstacles to the delivery without the use of a rubbing step of high performance LC-aligning materials.

Thus, a new photosensitive polyimide (PSPI) with cinnamate side groups has been synthesized to have a high T_g and is thus stable both thermally and dimensionally (Figure 19).⁷⁴ The PSPI was prepared by two step reactions; in the first step, a preimidized 6F-HAB PI was obtained from the isoquinoline-catalyzed polycondensation of 6F and 3,3'hydroxy-4,4'-diaminobiphenyl (HAB) and subsequent imidization in dry NMP; in the second step the 6F-HAB-CI PSPI was synthesized from the reaction of the 6F-HAB PI and cinnamoyl chloride. Its photoreactivity in nanoscaled films was investigated by ultraviolet-visible (UV-Vis), infrared (IR), Raman, and nuclear magnetic resonance (NMR) spectroscopies.⁷⁴ The LPUVL-induced alignment characteristics of the PSPI film were determined by optical retardation as well as by polarized UV-Vis and IR spectroscopies.⁷⁴

For the PSPI films irradiated with LPUVL, the dichroic ratio



Figure 19. Synthetic scheme for the photoreactive polyimide, 6FDA-HAB-CI PSPI.



Figure 20. UV dichroic ratios determined for 6F-HAB-CI PSPI films exposed to LPUVL (260-380 nm) with varying exposure energy.

 $[= (A_{\perp} - A_{\perp})/(A_{\perp} + A_{\perp})]$ was calculated from the absorbance A_{\perp} at the maximum absorption wavelength (λ_{max}), as measured with UV-Visible light linearly polarized perpendicular to the polarization direction of the LPUVL, and $A_{//}$, as measured with UV-Visible light linearly polarized parallel to the polarization direction of the LPUVL. The calculated dichroic ratios are displayed in Figure 20. As shown in the figure, these values are all positive for exposure energies $\leq 3.0 \text{ J/cm}^2$. The dichroic ratio increases rapidly with increasing exposure energy up to 0.5 J/cm² and then very slowly increases with further increases in the exposure energy. These results indicate that the CI chromophores located parallel to the polarization direction of the incident LPUVL are consumed more rapidly than those positioned perpendicular to the polarization direction of the LPUVL. Thus the directionally selective photoreaction of CI chromophores in the PSPI films due to LPUVL exposure induces a preferential orientation of the unreacted CI chromophores along the direction perpendicular to the polarization of the LPUVL. This preferential orientation is easily obtained with a LPUVL exposure energy of only 0.5 J/cm².

The molecular orientations in LPUVL-irradiated PSPI films were further investigated by using transmission FTIR spectroscopy with a linearly polarized IR light source and measuring the absorbance as a function of the angle of rotation of the films. This procedure enables to deduce the extents of the orientations of the unreacted CI chromophores and of the polymer chain backbones. The vinylene C=C stretching band at 1633 cm⁻¹ was found to be less intense when the polarization of the incident IR beam is at angles in the ranges 340-30 and 160-210° with respect to the polarization direction of the LPUVL used in the exposure. This result indicates that the CI chromophores with vinylene units positioned parallel to and in the vicinity of the polarization direction of the LPUVL are consumed more rapidly by photoreaction than those positioned at other orientations

in the film. Moreover, this result suggests that the LPUVL exposure induces a directionally selective photoreaction of the vinylene units in the CI side groups, although the directional photoreaction selectivity of the LPUVL is not high. Thus this selective photoreaction induces a preferentially molecular orientation of the vinylene C=C bonds of unreacted CI chromophores in directions defined by the angle ranges 50-140 and 230-325° with respect to the polarization direction (0° \leftrightarrow 180°) of the LPUVL.

The imide N-C stretching band at 1377 cm⁻¹ is more intense when the polarization of the incident beam is perpendicular to the polarization of the LPUVL. This result indicates that the imide N-C bonds are oriented by the LPUVL exposure to an alignment perpendicular to the polarization of the LPUVL. The imide N-C bonds are part of the PSPI main chain, so this result provides information on the orientation of the PSPI chains induced by LPUVL exposure.

Figure 21(a) displays a polar diagram of the transmitted



Figure 21. (a) Polar diagram of the transmitted light intensity [= (in-plane birefringence) \times (phase)] as a function of the angle of rotation of the film observed in the optical phase retardation measurements of a 6F-HAB-CI PSPI film irradiated with linearly polarized UV light (LPUVL) (260-380 nm) at 0.5 J/cm². (b) Variation of the optical retardation [= (in-plane birefringence) \times (film thickness)] of a 6F-HAB-CI film irradiated with LPUVL (260-380 nm) with varying exposure energy.

light intensity [=(in-plane birefringence) × (phase)] as a function of the angle of rotation of the film, obtained from optical phase retardation measurements of a PSPI film irradiated with LPUVL at an exposure energy of 0.5 J/cm². This polar diagram shows that the irradiated film exhibits a maximum in transmitted light intensity along the direction $287 \leftrightarrow 107^{\circ}$, which is at an angle of 107° with respect to the polarization direction $(0 \leftrightarrow 180^{\circ})$ of the LPUVL used in the UV-exposure, but exhibits a minimum transmitted light intensity value along the direction $197 \leftrightarrow 17^{\circ}$, which is at an angle of 17° with respect to the polarization direction of the LPUVL. On the other hand, the PSPI films that were not irradiated exhibited isotropic polar diagrams of the transmitted light intensity in the optical retardation measurements.

In general, polymer chains in thin films have a strong tendency to orient in the film plane rather than randomly; this tendency toward in-plane orientation of polymer chains increases not only as the film becomes thinner but also as the polymer chain rigidity becomes greater.^{6,119,120} The 6F-HAB-CI polymer is somewhat rigid, so that in films around 100-200 nm thick the polymer chains will tend to align in the film plane. In-plane orientations of the PSPI polymers were confirmed even for 5.0 μ m thick films by prism coupling measurements as described earlier; the in-plane refractive index is always slightly larger than the out-of-plane refractive index. This refractive index anisotropy indicates that the PSPI is a positively birefringent polymer whose polarization is larger along the polymer chain axis than along the direction normal to the polymer chain axis.

Given that the PSPI chain is positively birefringent, the anisotropic form of the polar diagram indicates that the PSPI polymer chains are oriented preferentially along the direction at an angle of 107° to the polarization direction of the LPUVL used in the exposure. This preferential orientation direction is somewhat different to that of the imide N-C bonds as well as to that of the vinylene C=C bonds, both described above. These differences in orientation direction are attributed to the geometrical structure of the PSPI polymer. As shown in Figure 19, the polymer chain has a kink at every 6F moiety, and hence its long chain axis is not parallel to the N-C bond axis. The CI side groups are attached at an angle of around 60° or around 120° , rather than 0° or 90° with respect to the polymer main chain. Therefore the long axis of CI group and the vinylene bond axis are not parallel to that of the polymer chain. Because of this geometrical arrangement of the CI side groups and the polymer main chain, the selective photoreactions of the CI side groups by LPUVL might explain the orientation direction of the polymer chains shown in Figure 21(a).

In Figure 21(a), the optical retardation was determined from the maximum transmitted light intensity values along the direction $287^{\circ} \leftrightarrow 107^{\circ}$. The above determination of optical retardation for the PSPI films irradiated with LPUVL was extended to various exposure energies. The resulting retardation values are plotted in Figure 21(b) as a function of exposure energy. As shown in Figure 21(b), the retardation rapidly increases with exposure energy up to around 0.5 J/cm² and then slowly increases with further increases in the exposure energy. This result suggests that a preferential orientation of the PSPI polymer chains in films is induced by LPUVL exposure only at 0.5 J/cm², which is consistent with our conclusion from the dichroic UV-Vis spectroscopy measurements described above.

The LPUVL-irradiated films were found to homogeneously align LC molecules along a direction at an angle of 107° with respect to the polarization of the LPUVL. This LC alignment result, along with the conclusions in regard to the orientation of polymer chains in irradiated films, shows that the oriented polymer chains in the irradiated films interact anisotropically with LC molecules and align the LC molecules along the orientation direction of the polymer chains. This LC alignment process is principally governed in the irradiated PSPI films by the orientations of the polymer main chains and of the unreacted CI side groups, whose directionally anisotropic interactions contribute to the alignment of the LC molecules. This LC alignment was found to be thermally stable up to 200°C, approximately 20°C higher than the T_g of the film.

In summary, this study has revealed the homogeneous, uniaxial LC-aligning ability of 6F-HAB-CI PSPI. The properties of this PSPI make it a promising candidate material for use as an LC alignment layer in advanced LC display devices, in particular in devices with an in-plane switching mode that require as low as possible LC pretilt angles.

Surface Morphologies. The surface of a C4-PMDA-PDA PI film without rubbing is apparently covered with submicrometer-scaled spikes (see atomic force microscopy (AFM) imiages in Figure 22).^{65-68,190,191} When the film is examined at the nanoscale, the surface shows an orange-peel like morphology with a periodicity of around 600 nm. The root-mean-square (rms) roughness is 0.5 nm over the area of $5 \times 5 \mu m^2$. The surface morphology and roughness of the PI film derive mainly from the characteristics of the polymer chains that govern the aggregation and molecular ordering that occur during the drying and thermal imidization processes after spin-casting. Similar smooth surfaces were observed for the other Cn-PMDA-PDA PI films without rubbing.

However, quite different surface morphologies were observed when those films were rubbed. Figure 23(a) presents AFM images of the surface of a rubbed C4-PMDA-PDA PI film.^{65-68,190,191} As seen in Figure 23(a), microgroove lines, which are produced by the rubbing process, are aligned parallel to the rubbing direction.^{65-68,190,191} This AFM image is compared with those of the other rubbed Cn-PMDA-PDA PI films (Figure 23(b)-(d)).^{65-68,190,191} The surface roughness values along the rubbing direction of the area marked in Figure 2 for the rubbed C4-, C6- C7-, and C8-PMDA-PDA films were 2.2, 1.6, 4.0, and 3.4 nm respectively, whereas



Figure 22. AFM images and surface profiles of C4-PMDA-PDA PI films without rubbing.

the surface roughness values across the rubbing direction for the same region of the film surfaces were 3.4, 4.2, 7.2, and 3.7 nm.^{65-68,190,191} Overall, the microgrooves developed along the rubbing direction are much larger in size than the LC molecules, which have dimensions of ca. 2 nm (length) and 0.3 nm (diameter). The characteristics of the microgrooves on the rubbed film surfaces (i.e., microgroove shape, size, and size distribution, and periodicity of microgroove lines), vary depending on the length of the *n*-alkyl bristle end group in the PI.^{65-68,190,191}

PMDA-PDA PI, which corresponds to the backbone of all the PIs tested in this study, is very hard and brittle.^{6,119,120} In contrast, all of the PIs prepared in this study were relatively ductile, and the ductility increased with increasing length of the *n*-alkyl end group in the bristle. Based on these properties, the surface morphologies described above might correlate with the deformation response characteristics of the PI films to the shear force caused by contact with the fibers during the rubbing process, which depend on the length of the *n*alkyl end group of the bristle.

In the case of photoreactive 6F-HAB-CI PI film, the surface morphology resembles that of Cn-PMDA-PDA PI films without rubbing.⁷⁴ However, the surface of 6F-HAB-CI film was found to become smoother when the film was exposed to LPUVL.⁷⁴

Interactions of PIs with Liquid Crystal Probes.

Nonphotoreactive PIs: Figure 24 shows polar diagrams of the variation of the optical phase retardation with the angle of rotation of PI films rubbed at a rubbing density of 120 and coated with a Merck nematic LC.^{190.191} As is clear from Figure 24(a)-(c), the nematic LC (5CB: 4-*n*-pentyl-4'-



Figure 23. AFM images and surface profiles of Cn-PMDA-PDA PI films rubbed with a rubbing density of 120: (a) C4-PMDA-PDA PI; (b) C6-PMDA-PDA PI; (c) C7-PMDA-PDA PI; (d) C8-PMDA-PDA PI. The arrow in each AFM image denotes the rubbing direction.

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Rubbing on centre

Figure 24. Polar diagrams of the variation of retardation with the angle of rotation of the LC coated film in optical phase retardation measurements of rubbed C6-PMDA-PDA PI films coated with LC: (a) C4-PMDA-PDA PI; (b) C6-PMDA-PDA PI; (c) C7-PMDA-PDA PI; (d) C8-PMDA-PDA PI. The films were rubbed with a rubbing density of 120.

cyanobiphenyl) coated films of C4-PMDA-PDA, C6-PMDA-PDA and C7-PMDA-PDA PIs exhibit a maximum retardation along the direction $90^{\circ} \leftrightarrow 270^{\circ}$, which lies perpendicular to the rubbing direction.^{190,191} These results indicate that the LC molecules in contact with the rubbed film surfaces are induced homogeneously to align perpendicular to the rubbing direction. These LC alignments are quite different from those for conventional PI alignment layer materials.^{212,213}

In combination with the surface morphology results described above, these data show that the LC molecules are induced to align perpendicular to the grooves created along the rubbing direction, indicating that the alignment of LCs is not directly induced by the grooves but by other effects. This LC alignment is also perpendicular to the alignments of both the polymer main chains and the *n*-alkyl bristle end groups (i.e., *n*-butyl, *n*-hexyl and *n*-heptyl), which are oriented preferentially along the rubbing direction, but is parallel to the alignment of the phenyloxy bristle units, which are oriented perpendicular to the rubbing direction. The observed perpendicular alignments of the LC molecules therefore imply that the LC molecules are anchored to the rubbed film surface by their strong anisotropic molecular interactions with the oriented phenyloxy bristle units, which override the interactions with the polymer main chains and the *n*-alkyl bristle end groups (i.e., *n*-butyl, *n*-hexyl, and *n*-heptyl) as well as with the microgrooves that are created along the rubbing

direction, and align the LC molecules along the oriented phenyloxy bristle units.

As seen in Figure 24(d), the LC coated film of C8-PMDA-PDA PI, on contrary, exhibits a maximum retardation along the direction $180^{\circ} \leftrightarrow 0^{\circ}$, which lies parallel to the rubbing direction.^{190,191} This result indicates that the LC molecules in contact with the rubbed film surfaces are induced homogeneously to align parallel to the rubbing direction.

The C8-PMDA-PDA PI has the same backbone and phenyloxy bristle units as the other Cn-PMDA-PDA PIs (i.e., C4-PMDA-PDA, C6-PMDA-PDA, and C7-PMDA-PDA PIs), but has one to four more carbons in its *n*-alkyl bristle end groups.^{190,191} Thus the length of the *n*-alkyl bristle end group seems to play an important role in the alignment of LC molecules in contact with the rubbed surface; apparently the roles played by the polymer main chain and the phenyloxy bristle unit in LC alignment are redundant for these PIs. These results indicate that the critical length of the *n*alkyl bristle end group that governs a transition from perpendicular to parallel LC alignment on rubbed PI films is 8 carbons (i.e. as in the *n*-octyl end group).

In general, an LC molecule is composed of an aromatic mesogen and an aliphatic tail. The aromatic mesogens might favorably interact with the phenyl ring components of the PIs via π - π interactions, while the aliphatic tails might undergo van der Waals type interactions with the *n*-alkyl bristle end groups of the PIs. This van der Waals interaction might become more favorable as the *n*-alkyl bristle end group becomes longer. Thus the van der Waals interactions with the n-alkyl bristle end groups oriented parallel to the rubbing direction might hinder the perpendicular LC alignment that is driven by the perpendicularly oriented phenyloxy bristle units; these interactions are also in competition with the contributions of the parallel oriented polymer main chains and the grooves created along the rubbing direction to the anisotropic molecular interactions with LC molecules. The negative contributions of the oriented *n*-alkyl bristle end groups in ≤ 7 carbons are not large enough to alter the observed perpendicular LC alignments to a parallel LC alignment. However, the presence of oriented n-octyl bristle end groups does result in parallel LC alignment.

Taking the observed LC alignment into account, the crystal-rotation technique was used to determine the pretilt angle of the LCs along the direction perpendicular to the rubbing direction.^{190,191} The LCs in the cells fabricated with rubbed films of C6-PMDA-PDA and C7-PMDA-PDA PIs did not exhibit any pretilt angle outside the range 25 to 55°, as observed in LC cells fabricated with rubbed films of C4-PMDA-PDA PI. Outside this range, the LC pretilt angle could not be measured because of the limits of the measurement technique. It is suspected that the pretilt angles of LCs in contact with the rubbed films of these PIs along a direction perpendicular to the rubbing direction lie in the range 25-55°, depending upon the rubbing density. For comparison,

the LC in the cells fabricated with rubbed films of C8-PMDA-PDA PI exhibits a pretilt angle of 75°; namely, the rubbed C8-PMDA-PDA PI film induces a homeotropic LC alignment with a pretilt angle of 75° in which the main director projected to the film plane is parallel to the rubbing direction.

With the observed LC alignment in mind, twist nematic (TN) cells were prepared and used in measurements of the twist angle of the LC molecules with a UV-Vis spectroscopic technique.^{190,191} All the TN cells exhibited a twist angle of 90°, regardless of rubbing density. From this measured twist angle, the anchoring energies of the LC molecules on the rubbed films of all the PIs are estimated to be much greater than 1×10^{-3} J/cm².^{190,191} This anchoring energy is comparable to those found for the rubbing type PIs currently used in the LC display industry. These therefore indicate that both the perpendicular alignments of LC molecules on the rubbed films of C4-PMDA-PDA, C6-PMDA-PDA, and C7-PMDA-PDA PIs and the parallel alignment of LC molecules on the rubbed C8-PMDA-PDA PI film are very stable.

Photoreactive PIs: All the parallel LC (5CB) cells fabricated with 6F-HAB-CI PSPI films irradiated with LPUVL at various exposure energies were found by optical microscopy to be homogeneous throughout.⁷⁴ Figure 25 displays a representative polar diagram, which was constructed for an LC cell fabricated with a PSPI film irradiated with LPUVL at 0.5 J/cm^{2,74} As shown in the figure, the main director of the LC molecules lies along the direction $287 \leftrightarrow 107^{\circ}$, which is at an angle of 107° to the polarization direction $(0 \leftrightarrow 180^{\circ})$ of the LPUVL used in the UV-exposure. This result indicates that the LC molecules in contact with the film surface are induced to homogeneously align in a direction at an angle of 107° to the polarization of the LPUVL. The director of the LC alignment was same for the other PSPI films irradiated at various exposure energies in the range 0.1-5.0 J/cm².



Figure 25. Polar diagram of absorbances measured from a parallel LC cell assembled with a 6F-HAB-CI PSPI film irradiated with LPUVL (260-380 nm) at 0.5 J/cm², as a function of the angle of rotation of the LC cell.

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Here it is considered that the interactions between the LC molecules and the PSPI polymer chains might affect the alignment of the LC molecules.

Firstly, the 5CB molecule has a length of approximately 1.8 nm and a diameter of approximately 0.25 nm, which are smaller than the dimensions of the chemical repeat unit of the main chain backbone but slightly larger than those of the CI side group. Therefore, both the polymer main chains and the CI side groups in the PSPI film may influence the LC alignment on the film surface.

Secondly, it has been previously suggested that for conventional rubbing-type polyimide alignment layer materials the major intermolecular interaction between polyimide and LC molecules is the π - π interaction between the phenyl rings of the polymer and those of the LC molecule. Taking this into account, the main chain backbone, which has four phenyl rings per chemical repeat unit, should have stronger intermolecular interactions with the biphenyl ring of the LC molecule than do the two side groups, which have only two phenyl rings per chemical repeat unit (see Figure 19). Moreover, the main chain backbone has a biphenyl unit, as does the mesogen unit of the LC molecule. Thus the biphenyl units in the polymer main chain may be significantly involved in interactions with the LC molecules.

Thirdly, one can consider the unreacted CI side groups left by LPUVL exposure and their contribution to the intermolecular interactions of the polymer chains with the LC molecules. The vinylene C=C bonds of the unreacted CI chromophores in the film were found to orient into the orientations defined by the angles 50-140° and 230-325° to the polarization direction $(0 \leftrightarrow 180^{\circ})$ of the LPUVL, as described earlier. As shown in Figure 19, the axis of the vinylene C=C bond is at some angle, rather than 0° or 90°, to the long axis of the CI chromophores. Thus the direction of the oriented CI chromophores might lie along a direction at some angle, rather than 0° or 90° , to that of the oriented vinylene C=C bonds. In addition, the dichroic UV spectroscopy results suggest that the unreacted CI chromophores lie preferentially along a direction perpendicular to the polarization of the LPUVL. Collectively, the IR and UV results suggest that the unreacted CI chromophores are oriented in a direction that is not parallel to the polarization of the LPUVL. Such preferentially oriented CI chromophores might contribute positively to the observed LC alignment.

Finally, the preferential orientation of the polymer main chains and their contribution to the intermolecular interactions of the polymer chains with the LC molecules are considered. In the PSPI films irradiated with LPUVL, the polymer chains are preferentially oriented along the direction at an angle of 107° with respect to the polarization of the LPUVL, as determined in the optical retardation measurements above. The preferential orientation of the polymer chains leads to anisotropic interactions with adjoining LCs, which in turn leads to LC alignment along the orientation direction (i.e., at an angle of 107 ° with respect to the polarization of the LPUVL). As shown in Figure 21, the main director of the preferentially oriented polymer chains exactly coincides with the main director of the LC alignment. This is a good sign that the PSPI polymer chains oriented anisotropically by LPUVL exposure play a major role in alignment of the LC molecules in contact with the irradiated film.

Taking the orientations of molecular groups and their possible interactions with the LC molecules into account, it is concluded that the anisotropically oriented polymer main chains and the unreacted CI side groups work together to induce a homogeneously uniaxial alignment of LC molecules, although the oriented polymer main chains make the dominant contribution to the LC alignment.

This LC alignment at the irradiated 6F-HAB-CI PSPI films, which is induced mainly by anisotropic interactions with the oriented polymer main chains, is a significant departure from the LC alignment observed for PVCi and its derivatives reported so far,¹⁹⁷⁻²⁰² for which LC alignment is always induced mainly by anisotropic interactions with the unreacted CI chromophores.

For the LC cells, the pretilt angle of the LCs was determined along the director of the LC alignment in the cell by using the crystal-rotation technique. The LC pretilt angle was measured to be zero degree for the LC cells fabricated with the PSPI films irradiated at the position perpendicular to the incident LPUVL direction. Instead, the LC cells, which were prepared with the PSPI films irradiated at the position with a tilt angle of 45 ° with respect to the propagation plane of LPUVL, show a LC pretilt angle ranged from 0.05 to 0.15 °, depending on the exposure energy; the films irradiated at higher exposure energy gave larger LC pretilt angle.

The thermal stabilities of the anisotropically oriented polymer chains and their LC alignment ability were also examined. For these studies, a series of LC cells were prepared with PSPI films irradiated with LPUVL at 1.5 J/cm² and followed by thermal annealing from 100 to 200 °C via the following steps: 100 °C/10 min, 120 °C/10 min, 140 °C /10 min, 160 °C/10 min, 180 °C/10 min, and 200 °C/10 min. The directors of the alignments of LCs on these annealed PSPI films were found to be same as that for the unannealed PSPI film, regardless of the annealing history. In particular, for the films annealed above the T_g (181 °C), the LC alignment directors were the same as that of the unannealed film. Only very small changes in the LC pretilt angle α were observed. Collectively, these results indicate that the oriented polymer chains and CI side groups that induce LC alignment are thermally stable up to 200 °C, which is approximately 20 °C higher than the T_{g} of the film.

In summary, the LC alignment characteristics of the thermally stable 6F-HAB-CI PSPI make it a promising candidate material for use as an LC alignment layer in advanced LC display devices, in particular devices with an in-plane switching mode that require as low as possible LC pretilt angles.

Closing Remarks

As reviewed above, there were good research progresses in the characterizations of PI precursors and their imidization reactions and in the developments of dielectric, light-emitting, and LC-alignment-layer PIs.

The ODSC technique combined with NMR spectroscopy demonstrates its great power to quantitatively characterize the thermal properties and phase transitions of PI precursors. Further this technique can constract phase diagrams of PI precutrsors in solvents. On the other hand, the details of PIs' imidizaton reaction were successfully investigated by using time-resolved FTIR spectroscopy.

A variety of chemical modifications based on the incorporation of fluorine atoms have been attempted to reduce the dielectric constant of PIs with retaining all advantageous properties such as excellent mechanical properties, low thermal expansivity, low interfacial stress, and high chemical resistance. However, there is a limititation in the reduction of PI' dielectric constant via the chemical modification approach. Indeed, there is still a big challenge to develop PIs of a dielectric constant of less than 2.6. One possible alternative approach is incorporating nanoscale pores into PIs, producing nonporous PI dielectrics. Most PIs become mobile above their T_g . In addition, the nanopores in the PIs may experience high capillary pressure because of their nanoscale dimension. Due to both the molecular mobility of the PIs induced by thermal processing and the high capillary pressure, the pores in the PI dielectrics may collapse during post thermal processing of the PIs, including thermal cycles. Thus, pores in the PIs must be stable thermally and dimensionally.^{91,131,214-229} Taking this requirement, the creation of thermally, dimensionally stable nanopores in PI dielectric matrices remains a significant challenge.^{91,131,214-229}

The development of light-emitting PIs has been tried to fully utilize all advantageous properties of PI. However, a few light-emitting PIs were reported so far. Thus, there is still a big challenge in developing high performance lightemitting PIs.

The most recently developed application of PIs is LCalignment layer for LC flat-panel display devices. Several LC-alignment lalyer PIs were commercialized in 1990s and used in the LC display industry, which require rubbing process for the mass production of LC dislay devices. Up to date, the development of new PIs with high performance for LC-alignment has been continued. Most PI films found to induce LC alignment along the rubbing direction. In contrast, specifically designed PIs demonstrated an unusual ability to induce LC alignment perpendicular to the rubbing direction. On the other hand, much research effort has been exerted to understand the mechanism of LC alignment on the rubbed PI films. As a result, all factors including film surface texture and polymer segmental orientation were found to involve in the LC alignment in the contact with the PI film. In general, the molecular interactions of LCs with the polymer segments oriented by the rubbing process are much stronger than that of LCs with the film surface texture. This is clearly evident in the LC alignment induced by the PSPI films exposed to linearly polarized UV light.

However, the rubbing process of PI films has some shortcomings, such as dust generation, electrostatic problems, and poor control of rubbing strength and uniformity. Moreover this process has a serious limitation in the fabrication of very large area of PI films which are required in the mass production of large size of LC television. Thus, at the present PIs which can offer the possibility of rubbing-free production of LC aligning films are highly demanded in the LC display industry. As reviewed, one alternative of rubbing type of PIs is PSPI, which can retain all advantageous properties of rubbing type of PIs but be processible with polarized UV light. Some PSPI candidates were reported so far. Further development of high performance PSPIs is still demanded, which can meet all requirements in the mass production of LC display devices.

Acknowledgements. These studies were supported by the Korea Science and Engineering Foundation (National Research Lab Program: Contract No. 2005-01385) and by the Ministry of Education (BK21 Program).

References

- W. M. Edwards and I. M. Robinson, U.S. Patent 2,867,609 (1959).
- (2) J. A. Kreuz, U.S. Patent 3,271,366 (1966).
- (3) C. E. Sroog, Prog. Polym. Sci., 16, 561 (1991).
- (4) M. I. Bessonov and V. A. Zubkov (eds.), *Polyamic acids and Polyimides: Synthesis, Transformations, and Structure*, CRS, Boca Raton, LA, 1993.
- (5) K. L. Ghosh and K. L. Mittal (eds.), *Polyimides: Funda*mentals and Applications, Dekker, New York, 1996.
- (6) M. Ree, K. Kim, S. H. Woo, and H. Chang, J. Appl. Phys., 81, 698 (1997).
- (7) M. Ree, S. H. Woo, K. Kim, H. Chang, W. C. Zin, K. B. Lee, and Y. J. Park, *Macromol. Symp.*, **118**, 213 (1997).
- (8) S. Numata, K. Fujisaki, and N. Kinjo, *Polymer*, 28, 2282 (1987).
- (9) A. S. Argon and M. I. Bessonov, *Polym. Eng. Sci.*, **17**, 174 (1977).
- (10) H. Ishida, S. T. Wellinghoff, E. Baer, and J. L. Koenig, *Macromolecules*, 13, 826 (1980).
- (11) S. T. Wellinghoff, H. Ishida, J. L. Koenig, and E. Baer, *Macromolecules*, 13, 834 (1980).
- (12) J. R. Havens, H. Ishida, and J. L. Koenig, *Macromolecules*, 14, 1327 (1981).
- (13) M. Ree, D. Y. Yoon, and W. Volksen, J. Polym. Sci.; Part B: Polym. Phys., 29, 1203 (1991).
- (14) M. Ree, D. Y. Yoon, and W. Volksen, *Polym. Preprints*, **31**, 613 (1990).
- (15) S. Rojstaczer, M. Ree, D. Y. Yoon, and W. Volksen, J.

Macromol. Res., Vol. 14, No. 1, 2006

Polym. Sci.; Part B: Polym. Phys., 30, 133 (1992).

- (16) Y. Kim, M. Ree, T. Chang, C. S. Ha, T. L. Nunes, and J. S. Lin, J. Polym. Sci.; Part B: Polym. Phys., 33, 2075 (1995).
- (17) M. Ree, T. L. Nunes, and K.-J. R. Chen, J. Polym. Sci.; Part B: Polym. Phys., 33, 453 (1995).
- (18) J. K. Gillham and H. C. Gillham, Polym. Eng. Sci., 13, 447 (1973).
- (19) M. Kochi, S. Isoda, R. Yokota, and H. Kambe, J. Polym. Sci.; Part B: Polym. Phys., 24, 1619 (1986).
- (20) E. Butta, S. De Petris, and M. Pasquini, *J. Appl. Polym. Sci.*, 13, 1073 (1969).
- (21) W. Wrasidlo, J. Macromol. Sci.-Phys., B3, 559 (1972).
- (22) Y. Kim, W. H. Goh, T. Chang, C. S. Ha, and M. Ree, *Adv. Eng. Mater.*, 6, 39 (2004).
- (23) K. H. Choi, J. C. Jung, H. S. Kim, B. H. Sohn, W.-C. Zin, and M. Ree, *Polymer*, 45, 1517 (2004).
- (24) I. S. Chung, C. E. Park, M. Ree, and S. Y. Kim, *Chem. Mater.*, 13, 2801 (2001).
- (25) J. Yu, M. Ree, Y. H. Park, T. J. Shin, W. Cai, D. Zhou, and K.-W. Lee, *Macromol. Chem. Phys.*, **201**, 491 (2000).
- (26) M. Ree, T. J. Shin, T. L. Nunes, and W. Volksen, *Polymer*, 41, 2105 (2000).
- (27) J. Yu, M. Ree, T. J. Shin, X. Wang, W. Cai, D. Zhou, and K.-W. Lee, *Polymer*, **41**, 169 (2000).
- (28) J. Yu, M. Ree, T. J. Shin, X. Wang, W. Cai, D. Zhou, and K.-W. Lee, J. Polym. Sci.; Polym. Phys., 37, 2806 (1999).
- (29) S. I. Kim, T. J. Shin, M. Ree, G. T. Hwang, B. H. Kim, H. Han, and J. Seo, *J. Polym. Sci.; Part A: Polym. Chem.*, **37**, 2013 (1999).
- (30) H. Han, H. Chung, C. C. Gryte, T. J. Shin, and M. Ree, *Polymer*, 40, 2681 (1999).
- (31) M. Ree, T. J. Shin, Y.-H. Park, S. I. Kim, S. H. Woo, C. K. Cho, and C. E. Park, *J. Polym. Sci.*, *Polym. Phys.*, **36**, 1261 (1998).
- (32) H. Han, J. Seo, M. Ree, S. M. Pyo, and C. C. Gryte, *Polymer*, **39**, 2963 (1998).
- (33) M. Ree, T. J. Shin, S. I. Kim, S. H. Woo, and D. Y. Yoon, *Polymer*, **39**, 2521 (1998).
- (34) Y. Kim, E. Kang, Y. S. Kwon, W. J. Cho, C. Chang, M. Ree, T. Chang, and C. S. Ha, *Synth. Metals*, **85**, 1399 (1997).
- (35) M. Ree, Y.-H. Park, K. Kim, C. K. Cho, and C. E. Park, *Polymer*, **38**, 6333 (1997).
- (36) Y. Kim, W. K. Lee, W. J. Cho, C. S. Ha, M. Ree, and T. Chang, *Polym. Internl*, **43**, 129 (1997).
- (37) K.-W. Lee, A. Viehbeck, G. F. Walker, S. Cohen, P. Zucco, R. Chen, and M. Ree, J. Adhesion Sci. Technol., 10, 807 (1996).
- (38) Y. Kim, M. Ree, T. Chang, and C.S. Ha, *Polymer Bulletin*, 34, 175 (1995).
- (39) H. C. Lee, M. Ree, and T. Chang, Polymer, 36, 2215 (1995).
- (40) M. Ree, H. Han, and C. C. Gryte, *High Perform. Polymers*, 6, 325 (1994).
- (41) M. Ree, T. L. Nunes, and J. S. Lin, Polymer, 35, 1148 (1994).
- (42) M. Ree, S. Swanson, and W. Volksen, *Polymer*, **34**, 1423 (1993).
- (43) M. Ree, K. J. Chen, D. P. Kirby, N. Katzenellenbogen, and D. Grischkowsky, *J. Appl. Phys.*, **72**, 2014 (1992).
- (44) W. M. Robertson, G. Arjavalingam, G. Hougham, G. V.

Kopcsay, D. Edelstein, M. Ree, and J. P. Chapple-Sokol, *Electronics Lett.*, **28**, 62 (1992).

- (45) M. Ree, T. L. Nunes, G. Czornyj, and W. Volksen, *Polymer*, 33, 1228 (1992).
- (46) C. R. Moylan, M. E. Best, and M. Ree, J. Polym. Sci.; Part B: Polym. Phys., 29, 87 (1991).
- (47) M. Ree, T. J. Shin, Y. H. Park, H. Lee, and T. Chang, *Korea Polym. J.*, 7, 370 (1999).
- (48) G. Czornyj, M. Ree, W. Volksen, and D.Y. Yang, U.S. Patent 5,446,074 (1995).
- (49) M. Ree, K. Kim, and S. M. Pyo, Korea Patent 0242684 (1999).
- (50) M. Ree, W. Volksen, and D.Y. Yoon, U.S. Patent 5,302,851 (1994).
- (51) M. Ree, S. A. Swanson, W. Volksen, and D. Y. Yoon, U.S. Patent 4,954,578 (1990).
- (52) M. Ree, K. Kim, and S. M. Pyo, Korea Patent 0255613 (2000).
- (53) M. Ree, S. M. Pyo, and S. I. Kim, Korea Patent Application 1998-14242 (1998).
- (54) L. F. Thompson, C. G. Willson, and S. Tagawa (eds.), *Polymers for Microelectronics: Resists and Dielectrics (ACS. Symp. Ser.* Vol. 537), Am. Chem. Soc., Washington, DC., 1994.
- (55) A. Deutsch, M. Swaminathan, M. Ree, C. Surovic, G. Arjavalingam, K. Prasad, D. C. McHoerron, M. McAllister, G. V. Kopcsay, A. P. Giri, E. Perfecto, and G. E. White, *IEEE Trans. Comp. Packag. Manuf. Technol.: Part B: Adv. Packaging*, **17**, 486 (1994).
- (56) G. Czornyj, K. J. Chen, G. Prada-Silva, A. Arnold, H. A. Souleotis, S. Kim, M. Ree, W. Volksen, D. Dawson, and R. DiPietro, *Proc. Elect. Comp. Tech. (IEEE)*, **42**, 682 (1992).
- (57) L. Shao, T. S. Chung, G. Wensley, S. H. Goh, and K. P. Pramoda, *J. Membr. Sci.*, **244**, 77 (2004).
- (58) T. Suzuki and Y. Yamada, Polymer Bulletin, 53, 139 (2005).
- (59) Y. C. Wang, S. H. Huang, C. C. Huc, C. L. Li, K. R. Lee, D. J. Liaw, and J. Y. Lai, *J. Membr. Sci.*, **248**, 15 (2005).
- (60) Y. K. Kim, J. M. Lee, H. B. Park, and Y. M. Lee, J. Membr. Sci., 235, 139 (2004).
- (61) M. Ree, H. Han, and C.C. Gryte, J. Polym. Sci.; Part B: Polym. Phys. Ed., 33, 505 (1995).
- (62) H. Han, C.C. Gryte, and M. Ree, Polymer, 36, 1663 (1995).
- (63) M. Ree, K.-J. R. Chen, and G. Czornyj, *Polym. Eng. Sci.*, 32, 924 (1992).
- (64) H. Han and M. Ree, Korea Polym. J., 5, 152 (1997).
- (65) B. Chae, S.W. Lee, B. Lee, W. Choi, S. B. Kim, Y. M. Jung, J. C. Jung, K. H. Lee, and M. Ree, *J. Phys. Chem. B*, **107**, 11911 (2003).
- (66) S. W. Lee, S. I. Kim, B. Lee, H. C. Kim, T. Chang, and M. Ree, *Langmuir*, **19**, 10381 (2003).
- (67) B. Chae, S. W. Lee, B. Lee, W. Choi, S. B. Kim, Y. M. Jung, J. C. Jung, K. H. Lee, and M. Ree, *Langmuir*, **19**, 9459 (2003).
- (68) S. W. Lee, B. Chae, B. Lee, W. Choi, S. B. Kim, S. I. Kim, S.-M. Park, J. C. Jung, K. H. Lee, and M. Ree, *Chem. Mater.*, **15**, 3105 (2003).
- (69) S. J. Lee, J. C.Jung, S. W. Lee, and M. Ree, J. Polym. Sci., Polym. Chem., 42, 3130 (2004).

- (70) M. Ree, S. I. Kim, and S. M. Pyo, Korea Patent 0233876 (1999).
- (71) M. Ree, S. I. Kim, and S. W. Lee, Synth. Metals, 117, 273 (2001).
- (72) Y. Sakai, M. Ueda, A. Yahagi, and N. Tanno, *Polymer*, 43, 3497 (2002).
- (73) S. Morino, T. Yamashita, K. Horie, T. Wada, and H. Sasabe, *React. Funct. Polymers*, 44, 183 (2000).
- (74) S. W. Lee, S. I. Kim, B. Lee, W. Choi, B. Chae, S. B. Kim, and M. Ree, *Macromolecules*, **36**, 6527 (2003).
- (75) S. W. Lee, T. Chang, and M. Ree, *Macromol. Rapid Commun.*, **22**, 941 (2001).
- (76) M. Ree and S. W. Lee, Korea Patent 0340729 (2002).
- (77) S. W. Lee and M. Ree, *Mol. Cryst. Liq. Cryst.*, **368**, 4277 (2001).
- (78) M. Ree, S. W. Lee, and J.-H. Kim, *Mol. Cryst. Liq. Cryst.*, 368, 4271 (2001).
- (79) S. I. Kim, S. W. Lee, Y. H. Park, and M. Ree, *Mol. Cryst. Liq. Cryst.*, **349**, 275 (2000).
- (80) M. Ree, S. W. Lee, and J. H. Kim, Korea Patent 0348151 (2002).
- (81) M. Ree, S. W. Lee, H. H. Shin, M. S. Nam, and S. H. Park, U.S. Patent 6,770,335 B2 (2004).
- (82) M. Ree, S. W. Lee, H. H. Shin, M. S. Nam, and S. H. Park, U.S. Patent 6,793,987 B2 (2004).
- (83) S. M. Pyo, S. I. Kim, T. J. Shin, M. Ree, K. H. Park, and J. S. Kang, *Polymer*, 40, 125 (1998).
- (84) S. M. Pyo, S. I. Kim, T. J. Shin, M. Ree, K. H. Park, and J. S. Kang, *Macromolecules*, **31**, 4777 (1998).
- (85) T. J. Shin, H. K. Park, S. W. Lee, B. Lee, W. Oh, J.-S. Kim, S. Baek, Y.-T. Hwang, H.-C. Kim, and M. Ree, *Polym. Eng. Sci.*, 46, 1232 (2003).
- (86) H. K. Park and M. Ree, Synth. Metals, 117, 197 (2001).
- (87) M. Ree, S. I. Kim, S. M. Pyo, T. J. Shin, H. K. Park, and J. C. Jung, *Macromol. Symp.*, **142**, 73 (1999).
- (88) M. Ree, S. M. Pyo, S. I. Kim, and H. K. Park, Korea Patent 0263993 (2000).
- (89) S. I. Kim, T. J. Shin, S. M. Pyo, J. M. Moon, and M. Ree, *Polymer*, 40, 1603 (1999).
- (90) S. M. Pyo, S. I. Kim, T. J. Shin, Y. H. Park, and M. Ree, J. Polym. Sci.; Part A: Polym. Chem., 37, 937 (1999).
- (91) M. Ree, W. H. Goh, and Y. Kim, *Polymer Bulletin*, **35**, 215 (1995).
- (92) K. R. Carter, R. A. DiPietro, M. I. Sanchez, and S. A. Swanson, *Chem. Mater.*, **13**, 213 (2001).
- (93) A. Mochizuki, T. Fukuoka, M. Kanada, N. Kinjou, and T. Yamamoto, J. Photopolym. Sci. Technol., 15, 159 (2002).
- (94) K. Kim, Ph.D. Thesis, Pohang University of Science & Technology, 1997.
- (95) S. I. Kim, Ph.D. Thesis, Pohang University of Science & Technology, 1999.
- (96) S.-B. Park, H. Kim, W.-C. Zin, and J. C. Jung, *Macromolecules*, 26, 1627 (1993).
- (97) J. C. Jung and S.-B. Park, Polymer Bulletin, 35, 423 (1995).
- (98) J. C. Jung and S.-B. Park, J. Polym. Sci.; Part A: Polym. Chem., 34, 357 (1996).
- (99) H. Kim, J. C. Jung, and W.-C. Zin, Polymer, 37, 2573 (1996).

- (100) K. H. Lee and J. C. Jung, Polymer Bulletin, 40, 407 (1998).
- (101) S. W. Lee, S. I. Kim, Y. H. Park, M. Ree, K. H. Lee, and J. C. Jung, *Mol. Cryst. Liq. Cryst.*, **349**, 271 (2000).
- (102) T. Matsuura, M. Ishizawa, Y. Hasuda, and S. Nishi, *Macro-molecules*, 25, 3540 (1992).
- (103) K. Kim and M. Ree, J. Polym. Sci.; Part A: Polym. Chem., 36, 1755 (1998).
- (104) S. Numata, K. Fujisaki, and N. Kinjo, *Polymer*, 28, 2282 (1987).
- (105) W. H. Goh, K. Kim, and M. Ree, *Korea Polym. J.*, 6, 241 (1998).
- (106) S. M. Pyo, T. J. Shin, S. I. Kim, and M. Ree, *Mol. Cryst. Liq. Cryst.*, **316**, 353 (1998).
- (107) E. Sacher, J. Macromol. Sci.; Phys. B, 25, 405 (1986).
- (108) R. W. Snyder and C. W. Sheen, Appl. Spect., 42, 655 (1988).
- (109) S. E. Molis, R. Saraf, and R. T. Hodgson, ANTEC-Conf. Proc., 37, 1700 (1991).
- (110) C. A. Pryde, J. Polym. Sci.; Part A: Polym. Chem., 27, 711 (1989).
- (111) S. I. Kim, S. M. Pyo, and M. Ree, *Macromolecules*, **30**, 7890 (1997).
- (112) S. I. Kim, S. M. Pyo, K. Kim, and M. Ree, *Polymer*, **39**, 6489 (1998).
- (113) E. Jenckel and R. Heusch, Kolloid-Z., 130, 89 (1953).
- (114) I. Uemastu and K. Honda, *Reports Prog. Polym. Phys. Jpn.*, 10, 245 (1966).
- (115) W. Kuhn, Kolloid-Z., 76, 258 (1936).
- (116) T. M. Birshtein, V. A. Zubkov, I. S. Milevskaya, V. E. Eskin, I. A. Baranovskaya, M. M. Koton, V. V. Kudryavtsev, and V. P. Sklizkova, *Eur. Polym. J.*, **13**, 375 (1977).
- (117) P. Flory, Statical Mechanics of Chain Molecules, Wiley & Sons, New York, 1969.
- (118) S. I. Kim, T. J. Shin, and M. Ree, Polymer, 40, 2263 (1999).
- (119) M. Ree, C. W. Chu, and M. J. Goldberg, *J. Appl. Phys.*, **75**, 1410 (1994).
- (120) M. Ree, T. J. Shin, and S. W. Lee, *Korea Polym. J.*, **9**, 1 (2001).
- (121) K. Kim, J. H. Ryou, Y. Kim, M. Ree, and T. Chang, *Polymer Bulletin*, 34, 219 (1995).
- (122) T. J. Shin, B. Lee, H. S. Youn, K.-B. Lee, and M. Ree, *Lang-muir*, **17**, 7842 (2001).
- (123) T. J. Shin and M. Ree, *Macromol. Chem. Phys.*, **203**, 781 (2002).
- (124) B. Thomson, Y. Park, P. C. Painter, and R. W. Snyder, *Macromolecules*, **22**, 4159 (1989).
- (125) R. W. Synder, B. Thompson, B. Bartges, D. Czerniawski, and P. C. Painter, *Macromolecules*, 22, 4166 (1989).
- (126) J. Labadie, H. Lee, D. Boese, D. Y. Yoon, W. Volksen, P. Brock, Y. Y. Cheng, M. Ree, and K. R. Chen, *Proc. Elect. Comp. Tech.* (*IEEE*), **43**, 327 (1993).
- (127) M. Ree, W. H. Goh, J. W. Park, M. H. Lee, and S. B. Rhee, *Polymer Bulletin*, **35**, 129 (1995).
- (128) S. I. Kim, M. Ree, T. J. Shin, C. Lee, T.-H. Woo, and S. B. Rhee, *Polymer*, **41**, 5173 (2000).
- (129) H. Chang, K. Kim, M. Ree, and K.-W. Lee, *Macromol. Chem. Phys.*, **200**, 422 (1999).
- (130) T. J. Shin and M. Ree, Langmuir, 21, 6081 (2005).
- (131) M. Ree, J. Yoon, and K. Heo, J. Mater. Chem., 16, 685

Macromol. Res., Vol. 14, No. 1, 2006

(2006).

- (132) G. L. Slonimskii, A. A. Askadskii, and A. I. Kitaigorodski, *Vyskomol. Soyed.*, A12, 494 (1970).
- (133) S. Numata, S. Oohara, K. Fujisaki, J. Imaijumi, and N. Kinjo, J. Appl. Polym. Sci., 31, 101 (1986).
- (134) K. Yamada, T. Mitsutake, K. Hiroshima, and T. Kajiyama, Proc. 2nd SPSJ Int. Polym. Conf. Tokyo, Aug. 20, 1986, pp. 51.
- (135) H. G. Rogers, R. A. Gaudiana, W. C. Hollinsed, P. S. Kalyanaraman, J. S. Manello, C. McGowan, R. A. Minns, and R. Sahatjian, *Macromolecules*, **18**, 1058 (1985).
- (136) W. Groh and A. Zimmerman, *Macromolecules*, 24, 6660 (1991).
- (137) J. C. Maxwell, N. Philos. Trans., 155, 459 (1865).
- (138) C. C. Ku and R. Liepins (eds.), *Electrical Properties of Polymers: Chemical Principles*, Hanser, New York, 1987.
- (139) A. Kraft, A. C. Grimsdale, and A. B. Holmes, *Angew. Chem. Int. Ed.*, **37**, 403 (1998).
- (140) D. Y. Kim, H. N. Cho, and C. Y. Kim, Prog. Polym. Sci., 25, 1089 (2000).
- (141) E. I. Mal'tsev, V. I. Berendyaev, M. A. Brusentseva, A. R. Tameev, V. A. Kolesnokov, A. A. Kozlov, B. V. Kotov, and A. V. Vannikov, *Polymer Internl.*, **42**, 404 (1997).
- (142) E. I. Mal'tsev, M. A. Brusentseva, V. A. Kolesnokov, V. I. Berendyaev, B. V. Kotov, and A. V. Vannikov, *Appl. Phys. Lett.*, **71**, 3480 (1997).
- (143) A. Wu, T. Akagi, M. Jikei, M.-A. Kakimoto, Y. Imai, S. Ukishima, and Y. Takahashi, *Thin Solid Films*, **273**, 214 (1996).
- (144) H.-C. Kim, J.-S. Kim, K.-S. Kim, H.-K. Park, S. Baek, and M. Ree, J. Polym. Sci., Polym. Chem., 42, 825 (2004).
- (145) J. J. Kim, K.-S. Kim, S. Beak, H. Kim, and M. Ree, J. Polym. Sci., Polym. Chem., 40, 1173 (2002).
- (146) J.-S. Kim, H. K. Ahn, and M. Ree, *Tetrahedron Lett.*, 46, 277 (2005).
- (147) M. Ree, J.-S. Kim, J. J. Kim, J. Yoon, B. H. Kim, and H. Kim, *Tetrahedron Lett.*, 44, 8211 (2003).
- (148) M. Ree, H. K. Ahn, and H.-K. Park, Korea Patent 0335963 (2002).
- (149) M. Ree, H. K. Ahn, and J. J. Kim, Korea Patent 0367719 (2002).
- (150) Z. Yang, I. Sokolik, and F. E. Karasz, *Macromolecules*, 26, 1188 (1993).
- (151) J. C. de Mello, H. F. Wittmann, and R. H. Friend, Adv. Mater., 9, 230 (1997).
- (152) E. D. Wachsman and C. W. Frank, *Polymer*, **29**, 1191 (1988).
- (153) M. Hasegawa, H. Arai, I. Mita, and R. Yokota, *Polym. J.*, 22, 875 (1990).
- (154) J.-W. Yu and C. S. P. Sung, *Macromolecules*, **30**, 1845 (1997).
- (155) P. J. Collings and J. S. Patel, Eds. Handbook of Liquid Crystal Research, Oxford University Press, Oxford, 1997.
- (156) J. Cognard, Alignment of Liquid Crystals and Their Mixtures, Gorden & Breach, London, 1982.
- (157) S. W. Lee, B. Chae, S. G. Hahm, B. Lee, S.B. Kim, and M. Ree, *Polymer*, **45**, 4068 (2005).
- (158) S. W. Lee, H. C. Kim, B. Lee, T. Chang, and M. Ree, Mac-

romolecules, 36, 9905 (2003).

- (159) S. W. Lee, B. Chae, H. C. Kim, B. Lee, W. Choi, S. B. Kim, T. Chang, and M. Ree, *Langmuir*, **19**, 8735 (2003).
- (160) K.-W. Lee, S.-H. Paek, A. Lien, C. During, and H. Fukuro, *Macromolecules*, **29**, 8894 (1996).
- (161) S. I. Kim, M. Ree, T. J. Shin, and J. C. Jung, J. Polym. Sci.; Part A: Polym. Chem., 37, 2909 (1999).
- (162) J. H. Park, J. C. Jung, B. H. Sohn, S. W. Lee, and M. Ree, J. Polym. Sci., Polym. Chem., **39**, 3622 (2001).
- (163) J. H. Park, B. H. Sohn, J. C. Jung, S. W. Lee, and M. Ree, J. Polym. Sci., Polym. Chem., **39**, 1800 (2001).
- (164) S. W. Lee, S. I. Kim, Y. H. Park, M. Ree, K. H. Lee, and J. C. Jung, *Mol. Cryst. Liq. Cryst.*, **368**, 4327 (2001).
- (165) S. W. Lee, S. I. Kim, Y. H. Park, M. Ree, Y. N. Rim, H. J. Yoon, and Y. B. Kim, *Mol. Cryst. Liq. Cryst.*, **349**, 279 (2000).
- (166) S. I. Kim, T. J. Shin, M. Ree, and J. C. Jung, J. Soc. Inform. Display, 8, 61 (2000).
- (167) J. C. Jung, K. H. Lee, B. H. Sohn, S. W. Lee, and M. Ree, *Macromol. Symp.*, **164**, 227 (2001).
- (168) S. I. Kim, S. M. Pyo, M. Ree, M. Park, and Y. Kim, *Mol. Cryst. Liq. Cryst.*, **316**, 209 (1998).
- (169) N. B. Colthup, L. H. Daly, and S. E. Wiberiey, eds., *Introduction to Infrared and Raman Spectroscopy*, Academic, New York, 1996.
- (170) W. G. Dauben and W. W. Epstein, J. Org. Chem., 24, 1595 (1959).
- (171) L. J. Bellamy, B. R. Connelly, A. R. Philpotts, and R. L. Z. Williams, *Elektrochem.*, 64, 563 (1960).
- (172) D. W. Berreman, Phys. Rev. Lett., 28, 1683 (1972).
- (173) D. W. Berreman, Mol. Cryst. Liq. Cryst., 23, 215 (1973).
- (174) P. G. de Gennes, *Physics of Liquid Crystals*, W. Marshall and D. H. Wilkinson, Eds., Clarendon, Oxford, 1974, Chap. 3.
- (175) E. S. Lee, P. Vetter, T. Miyashita, T. Uchida, M. Kano, M. Abe, and K. Sugawara, *Jpn. J. Appl. Phys.*, **32**, L1436 (1993).
- (176) A. J. Pidduck, G. P. Bryan-Brown, S. Haslam, R. Bannister, I. Kitely, T. J. McMaster, and L. Boogaard, *J. Vac. Sci. Technol. A*, 14, 1723 (1996).
- (177) J. Kim and S. Kumar, Phys. Rev. E, 57, 5644 (1998).
- (178) T. Uchida, M. Hirano, and H. Sakai, *Liq. Cryst.*, **231**, 95 (1989).
- (179) J. A. Castellano, Mol. Cryst. Liq. Cryst., 94, 33 (1983).
- (180) M. E. Becker, R. A. Killan, B. B. Kosmowski, and D. A. Mlynski, *Mol. Cryst. Liq. Cryst.*, **132**, 167 (1986).
- (181) V. G. Nazarenko and O. D. Lavrentovich, *Phys. Rev. E.*, 49, R990 (1994).
- (182) D. Johannsmann, H. Zhou, P. Sonderkaer, H. Wierenga, B. O. Myrvold, and Y. R. Shen, *Phys. Rev. E*, **48**, 1889 (1993).
- (183) G. Durand, *Physica A*, **163**, 94 (1990).
- (184) G. Barbero, L. R. Evangelista, and N. V. Madhusudana, *Eur. Phys. J.*, **1**, 327 (1998).
- (185) T. Sugiyama, S. Kuniyash, D.S. Seo, F. Hiroyoshi, and S. Kobayashi, *Jpn. J. Appl. Phys.*, **29**, 2045 (1990).
- (186) K. Sakamoto, R. Arafune, N. Ito, S. Ushioda, Y. Suzuki, and S. Morokawa, *Jpn. J. Appl. Phys.*, **33**, L1323 (1994).
- (187) K. Sakamoto, R. Arafune, and S. Ushioda, Appl. Spectrosc.,

51, 541 (1997).

- (188) R. Arafune, K. Sakamoto, S. Ushioda, S. Tanioka, and S. Murata, *Phys. Rev. E*, **58**, 5914 (1998).
- (189) K. Sakamoto, R. Arafune, N. Ito, S. Ushioda, Y. Suzuki, and S. Morokawa, *J. Appl. Phys.*, **80**, 431 (1996).
- (190) B. Chae, S. B. Kim, S. W. Lee, S. I. Kim, W. Choi, B. Lee, M. Ree, K. H. Lee, and J. C. Jung, *Macromolecules*, **35**, 10119 (2002).
- (191) S. W. Lee, S. J. Lee, S. G. Hahm, T. J. Lee, B. Lee, B. Chae, S. B. Kim, J. C. Jung, W. C. Zin, B. H. Sohn, and M. Ree, *Macromolecules*, **39**, 4331 (2005).
- (192) S.W. Lee and M. Ree, J. Polym. Sci., Polym. Chem., 42, 1322 (2004).
- (193) B. Chae, S. W. Lee, S. B. Kim, B. Lee, and M. Ree, *Lang-muir*, **19**, 6039 (2003).
- (194) B. Chae, S. W. Lee, Y. M. Jung, M. Ree, and S. B. Kim, *Langmuir*, **19**, 687 (2003).
- (195) B. Chae, S. W. Lee, M. Ree, and S. B. Kim, *Vibrational Spectro.*, **29**, 69 (2002).
- (196) M. Ree, S. W. Lee, and W. Choi, Korea Patent 0499270 (2005).
- (197) M. Schadt, K. Schmitt, V. Kozinkov, and V. Chigrinov, *Jpn. J. Appl. Phys.*, **31**, 2115 (1992).
- (198) M. Schadt, M. Seiberle, A. Schuster, and S. M. Kelly, *Jpn. J. Appl. Phys.*, **34**, L764 (1995).
- (199) M. Schadt, H. Seiberle, and A. Schuster, *Nature*, **381**, 212 (1996).
- (200) M. O'Neill and S. M. Kelly, J. Phys. D: Appl. Phys., 33, R67 (2000).
- (201) K. Ichimura, Chem. Rev., 100, 1847 (2000).
- (202) K. Ichimura, Y. Akita, H. Akiyama, K. Kudo, and Y. Hayashi, *Macromolecules*, **30**, 903 (1997).
- (203) Y. Iimura, S. Kobayashi, T. Hashimoto, T. Sugiyama, and K. Katoh, *HEICE Trans. Electron. E*, **39**, 1040 (1996).
- (204) K. Y. Han, B. H. Chae, S. H. Yu, J. K. Song, J. G. Park, and D. Y. Kim, AM-LCD'96/IDW'96, 403 (1996).
- (205) M. Vilfan, I. D. Olenik, A. Mertelj, and M. Copic, *Phys. Rev. E*, **63**, 061709 (2001).
- (206) N. Klopcar, I. D. Olenik, M. Copic, M. W. Kim, A. Rastegar, and Th. Rasing, *Mol. Cryst. Liq. Cryst.*, **368**, 395 (2001).
- (207) X. T. Li, D. H. Pei, S. Kobayash, and Y. Iimura, Jpn. J. Appl. Phys., 36, L432 (1997).
- (208) J.-W. Lee, H.-T. Kim, S.-J. Sung, and J.-K. Park, Synth. Metals, 117, 267 (2001).
- (209) E. J. Kim, O O. Park, L. H. Feng, Y. Kawanami, H. Furue, and S. Kobayashi, AM-LCD'97/IDW'97, 105 (1997).
- (210) R. Yamaguchi, Y. Goto, and S. Sato, Jpn. J. Appl. Phys., 41, L889 (2002).
- (211) L. M. Minsk, J. G. Smith, W. P. van Deusen, and J. F. Wright, J. Appl. Polym. Sci., 2, 302 (1958).
- (212) Y. B. Kim, H. Olin, S. Y. Park, J. W. Choi, L. Komitov, M. Matuszczyk, and S. T. Lagerwall, *Appl. Phys. Lett.*, **66**, 2218 (1995).
- (213) Y. B. Kim and B. S. Ban, Liquid Crystals, 26, 1579 (1999).
- (214) B. Lee, W. Oh, J. Yoon, Y. Hwang, J. Kim, B. G. Landes, J. P. Quintana, and M. Ree, *Macromolecules*, **38**, 8991 (2005).
- (215) J.-S. Kim, H.-C. Kim, B. Lee, and M. Ree, Polymer, 46,

7394 (2005).

- (216) B. Lee, J. Yoon, W. Oh, Y. Hwang, K. Heo, K. S. Jin, J. Kim, K.-W. Kim, and M. Ree, *Macromolecules*, 38, 3395 (2005).
- (217) B. Lee, W. Oh, Y. Hwang, Y.-H. Park, J. Yoon, K. S. Jin, K. Heo, J. Kim, K.-W. Kim, and M. Ree, *Adv. Mater.*, **17**, 696 (2005).
- (218) B. Lee, Y.-H. Park, Y.-T. Hwang, W. Oh, J. Yoon, and M Ree, *Nat. Mater.*, 4, 147 (2005).
- (219) W. Oh, Y.-T. Hwang, Y. H. Park, M. Ree, S.-H. Chu, K. Char, J. K. Lee, and S. Y. Kim, *Polymer*, 44, 2519 (2003).
- (220) J. Bolze, M. Ree, H. S. Youn, S. H. Chu, and K. Char, *Lang-muir*, 17, 6683 (2001).
- (221) M. Ree and W. Oh, Korea Patent 0397372 (2003).
- (222) M. Ree and W. Oh, Korea Patent Application 2000-53707

(2000).

- (223) M. Ree and W. Oh, Korea Patent 0378253 (2003).
- (224) M. Ree, W. Oh, Y. Hwang, and B. Lee, *PCT/KR*2004/ 002104 (2004).
- (225) M. Ree, J.-S. Kim, B. Lee, J. Yoon, and K. S. Jin, *PCT/ KR*2005/001053, April 12, 2005.
- (226) M. Ree, W. Oh, Y. Hwang, and B. Lee, Korea Patent Application 2003-0041384 (2003).
- (227) M. Ree, W. Oh, Y. Hwang, and B. Lee, *PCT/KR*2004/ 000316, July 15, 2004.
- (228) M. Ree, W. Oh, Y. Hwang, and B. Lee, German Patent Application 112004000058.0 (2005).
- (229) M. Ree, J.-S. Kim, B. Lee, H. Yoon, K.S. Jin, and K. Heo, *PCT/KR*2005/001053, April, 12, 2005.