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Novel Polypyromellitimides and Their Liquid Crystal Aligning Properties

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SUMMARY: Various aromatic poly{3,6-bis[(4-n-alkyloxy)phenyloxy]-pyromellitimide}s [poly(Ar-C_m-PMDA)s, m = 1, 4, 8, 12] were prepared in film form by routine two-step condensation of 3,6-bis[(4-n-alkyloxy)phenyloxy]pyromellitic dianhydrides (C_m-PMDAs) with various aromatic diamines. After characterization of their chemical structures their solution, thermal and liquid crystal (LC)-aligning properties in terms of pretilt angle at various rubbing densities were measured and discussed with respect to their backbone structures. All polyimide films showed excellent thermal stability and homogeneous LC alignment, but the poly(p-phenylene-C_{12}-PMDA) exhibited completely homeotropic alignment while the pretilt angle values of poly(p-phenylene-C_8-PMDA) varied with varying rubbing density.

Introduction

One of the recently developed, very important applications of aromatic polyimides is their use as LC-aligning layers for flat-panel LC display devices[1-3] for mobile phones and computers and TV monitors, in which the twisted (90°) or the supertwisted (270°) thin-film transistor LC display mode is adopted. Polyimides are used as LC-aligning

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layers, because they have excellent transparency, heat resistance, adhesiveness, dimensional stability and insulation ability[4]. Such polyimide film surfaces are rubbed with a cellulose fabric to attain alignment of LC molecules with certain degree of pretilt angle values[5]. These values play the most important role[1] in tailoring optical and electrical performance of today's industrial LC display devices which currently use nematic LC molecules.

Although the exact mechanism of the interaction between LC molecules and polyimide chains on rubbed surfaces has not been unambiguously elucidated yet and is still disputed between the microgroove mechanism[6] and the polymer chain reorientation mechanism[7-9], the rubbing is the only technique that is adopted in industry for mass-production of flat-panel LC display devices, and it is commonly accepted[10-12] that rubbed surfaces of the polyimide with flexible side chains result in high pretilt angle values.

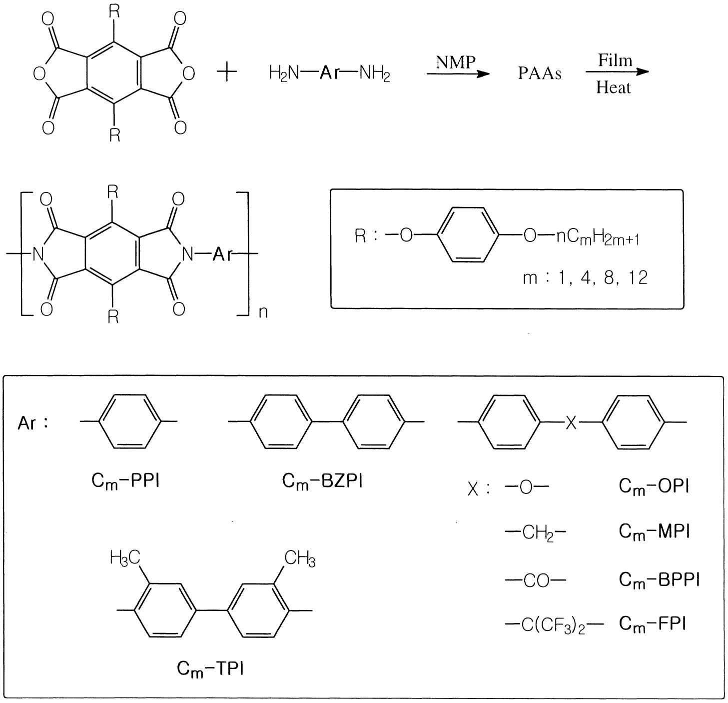

Fig. 1. Preparation and structure of the polyimides

Side chains can be attached to polyimide main chains, either to the diamine unit or to the dianhydride unit. Till present a number of the former case[14-19] but only few examples of the latter case have been reported. Although pyromellitic dianhydride is one of the most representative dianhydride monomers in synthesis of aromatic polyimides, the incorporation of only short substituents such as phenyl[20-22], methyl[23], phenyloxy[24], halogen[25,26] and trifluoromethyl[27] in 3- and 6-position has been filed in the literature. In our previous work[28] the first report on monomeric 3,6-bis[4-(n-alkyloxy)phenyloxy]-modified pyromellitic dianhydrides C_m-PMDAs (m = 1, 4, 8, 12) and their polyimides with 4,4'-oxydi(aniline) has been presented.

In the present contribution polyimides of C_m-PMDAs with various other aromatic diamines are introduced and their LC-aligning properties are discussed. In Fig. 1 it is shown that C_m-PMDAs were polymerized with p-phenylenediamine (PPD), benzidine-4,4'-diamine (BZ), o-tolidine, 4,4'-methylenedi(aniline) (MDA), benzo-phenone-4,4'-diamine (BPDA) and hexafluoroisopropylidene-4,4'-di(aniline) (FDA) and the polyimides obtained from them are coded as C_m-PPIs, C_m-BZPIs, C_m-TPIs, C_m-MPIs, C_m-BPPIs, C_m-FPIs, respectively. Fig. 1 also includes the polyimide from 4,4'-oxydi(aniline) (ODA) and C_m-PMDAs to cover a wider range of discussion.

Experimentals

Synthesis. Monomeric C_m-PMDAs were prepared according to our previous work[28] and their polymerizations were conducted by the routine two-step procedure in NMP at room temperature. The polyimide films were obtained by casting the poly(amic acid)s from NMP solutions onto glass plates, followed by vacuum-drying at 80 °C for 2 h and heating in vacuum at 130 °C for 1 h, 200 °C for 2 h and 300 °C for 30 min. Some samples were imidized with acetic anhydride (Ac_2O).

Rubbing density measurement[13,29]**.** The polyimide films on glass substrates were rubbed using a laboratory rubbing machine (Wande Co.) with a roller covered by a rayon cloth (Yoshikawa Co., YA-20-R) and the rubbing density *L/l* was calculated according to the equation (1) :

$$\frac{L}{l} = N\left(\frac{2\pi rn}{60v} - 1\right) \qquad (1)$$

where L is the total length (mm) of the rubbing cloth that contacts a certain point of the polymer film, l is the contact length (mm) of circumference of rubbing roller, N is the cumulative number of rubbings, n is the speed (rpm) of rubbing roller, r is the radius (cm) of roller, and v is the velocity (cm/s) of the substrate stage.

Pretilt angle determination : Two pieces of the rubbed substrates were assembled in the anti-parallel rubbing direction using 50 μm thick poly(ethylene terephthalate) film spacers. A nematic LC, 4-(*n*-pentyl)-4'-cyanobiphenyl (CB) (Aldrich Company) containing 1.0 wt % Disperse Blue1 (1,4,5,8-tetraamino-9,10-anthraquinone) as a dichroic dye was injected into the cell gap, followed by sealing the injection hole with an epoxy glue. The pretilt angle (θ_p) was measured by the crystal rotation method using a laboratory apparatus[30] and the LC alignment direction was examined by measuring the absorbencies of the linearly polarized He-Ne laser beam (632.8 nm) as a function of the rotational angle.

Results and discussion

Synthesis. Various aromatic polyimides with flexible n-alkyloxy side chains were prepared in film form by two-step condensation of 3,6-bis[4-(n-alkyloxy)phenyloxy]-pyromellitic dianhydrides with various aromatic diamines in NMP at room temperature and thermal treatment of the films cast on glass plates from the corresponding poly(amic acid)s, as shown in Fig. 1. The C_m-PMDAs were synthesized[28] as previously reported.

The polyimides synthesized were characterized by various spectroscopic methods and elemental analysis, and it was confirmed that their chemical structures were in good agreement with the structures depicted in Fig. 1.

Solution properties. All the polyimide films obtained by thermal imidization were insoluble in organic solvents whereas most of them imidized with acetic anhydride were soluble in NMP. The fully rigid poly{p-phenylene-3,6-[4-(n-alkyloxy)phenyloxy]-pyromellitimide}s (C_m-PPIs) were completely insoluble in all organic solvents or even

Tab. 1. Inherent viscosities[a)] of the polyimides in NMP at 25 °C

m	C_m-PPI[b)]	C_m-BZPI	C_m-TPI	C_m-OPI	C_m-MPI
1	0.43	-	-	0.51	0.66
4	0.81	2.29	0.56	0.68	0.53
8	0.95	-	0.66	0.66	0.64
12	0.40	-	0.56	0.46	0.53

a) Measured at a concentration of 0.1 g/dL

b) Values for PAAs

in concentrated H_2SO_4 or methanesulfonic acid, and inherent viscosities could only be determined for the respective poly(amic acid)s. Under the poly{p-biphenylene-3,6-[4-(n-alkyloxy)-phenyloxy]pyromellitimide}s (C_m-BZPIs) only the polyimide with $m = 4$ was completely soluble in NMP, which was found to be generally the best solvent.

In Tab. 1 inherent viscosities of the chemically imidized polyimides are summarized. It shows that all polyimides have sufficiently high viscosities, and hence high molecular weights. It also shows that the polymers with $m = 12$ have generally lower inherent viscosity than the others, meaning that the n-dodecyl group is so bulky that free approach of diamine monomer molecules to the anhydride carbonyl group could be hindered to some extent.

Phase transition. The phase transitions of polyimides were studied with DSC at 10 °C/min scan rate in nitrogen atmosphere. Polyimides with rigid-rod backbone structure such as C_m-PPIs, C_m-BZPIs and C_m-TPIs did not show any transition even after prolonged annealing and repeated scanning.

Tab. 2. Phase transitions (°C) of the as-polymerized polyimides

m	C_m-OPI		C_m-MPI		C_m-BPPI		C_m-FPI	
	T_g	T_m	T_g	T_m	T_g	T_m	T_g	T_m
1	302	-	308	-	301	-	307	-
4	279	-	263	-	268	-	298	-
8	238	345	192	333	258	312	196	-
12	217	340	185	314	264	320	171	-

The other polymers gave phase transition temperatures, which are summarized in Tab. 2. Tab. 2 shows first that C_m-FPIs are completely amorphous regardless of side chain length while C_m-OPIs, C_m-MPIs and C_m-BPPIs have both glass and melting transitions when $m \geq 8$. It is, however, quite surprising that C_m-OPIs, C_m-MPIs and C_m-BPPIs with $m \geq 8$ possess melting transitions because the basic unit of these polymers contains a tetrahedrally (MPI) or triangularly (OPI and BPPI) bent unit between two p-phenylene units. More surprising is that melting peaks of Ac_2O-imidized C_{12}-OPIs and C_{12}-BPPIs do not reappear in the second heating scan, whereas the melting peak of Ac_2O-imidized C_{12}-MPI was perfectly reproducible even in repeated scans, as shown in Fig. 2. The

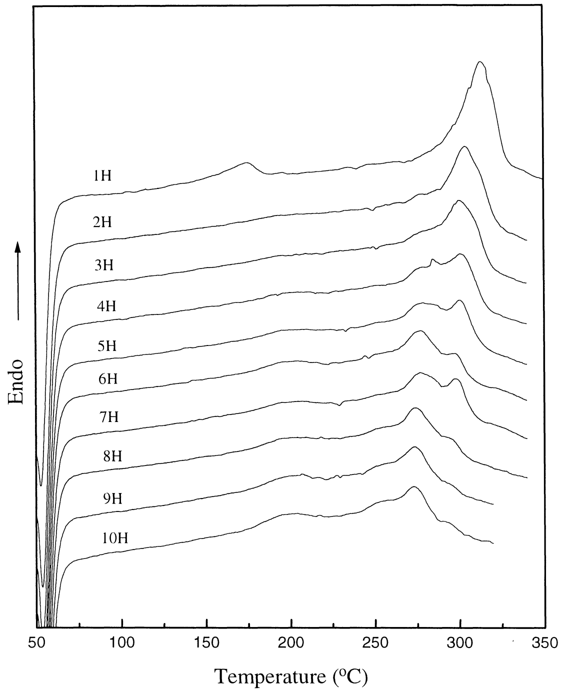

Fig. 2. DSC heating scans of C_{12}-MPI.

only difference to point out here related to the chemical structure between the two categories is that in C_m-OPIs and C_m-BPPIs the two p-phenylene rings are in π-electronic conjugation, though low in extent, while in C_m-MPIs such conjugation is completely excluded. However, the thermally imidized C_{12}-MPI did not show reproducibility of melting and behaved like C_m-OPIs and C_m-BPPIs. This difference between thermally imidized and chemically imidized samples should be studied more detailedly.

Tab. 2 also shows that phase transition temperatures decrease with increasing side chain length, indicating that the degree of internal plasticization increases.

Thermal stability. Thermal resistances of the polymers were examined by TGA at 10 °C/min scan rate in nitrogen atmosphere and expressed in terms of temperature of 5% weight loss ($T_{5\%}$). The $T_{5\%}$ values are summarized in Tab. 3.

Tab. 3. Themal stability ($T_{5\%}$) of the polyimides

m	C_m-PPI	C_m-BZPI	C_m-TPI	C_m-OPI	C_m-MPI	C_m-BPPI	C_m-FPI
1	470	467	–	454	450	465	470
4	460	461	447	453	444	465	456
8	451	452	442	442	439	448	456
12	450	450	446	438	437	438	450

Tab. 3 shows that C_m-PPI, C_m-BZPI and C_m-FPI have the highest and roughly the same resistance. Such excellent values arise either from the rigid backbone structure (C_m-PPI and Cm-BZPI) or from high dipolar interactions (C_m-FPI). Due to π-conjugation the backbone of C_m-PPI and C_m-BZPI is so rigid that the side chain content up to n-dodecyl is not high enough for internal plasticization, and these polymers show no T_g or T_m and a two-step pyrolysis behavior was observed in TGA. C_m-TPI is also a rigid-backbone polymer, and hence it does not show any phase transition, but, at sufficiently high temperatures around which chain degradation takes place, its methyl groups cause an additional plasticization for its main chain to degrade more easily.

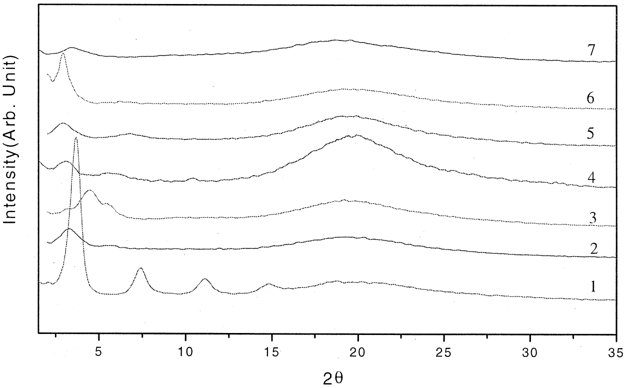

Fig. 3. WAXS diffractogram of C_{12}-polyimide films.
1: PPI, 2: BZPI, 3: TPI, 4: OPI, 5: MPI, 6: BPPI, 7: FPI

Crystalline structure. Crystalline morphologies of the polyimide film samples were examined by wide-angle X-ray diffraction at room temperature and the diffractograms obtained from C_{12}-PMDAs are shown in Fig. 3. It shows that the crystallinity depends strongly on the backbone rigidity of the polymers. The more rigid the backbones are, the better layered-crystalline structures are developed and the higher is the crystallinity. Therefore, C_{12}-PPI has the highest crystallinity and the best-developed layered-crystal structure.

The non-rigid polyimides containing bent structures in their diamine unit are only low in crystallinity with very loosely developed layered structure like in C_m-OPIs, C_m-MPIs and C_m-BPPIs or are completely amorphous like C_m-FPIs. Reproducible formation and disruption of such loose crystalline structure as observed in the Ac_2O-imidized C_{12}-MPI during thermal treatment, (See Fig. 2) draws a particular interest and requires further detailed structural studies.

Liquid-crystal alignment. To measure LC alignability of the polyimides, standard cells were made from two 1 cm x 1 cm polyimide films whose rubbing directors were aligned antiparallel and one 50 μm thick poly(ethylene terephthalate) film and 5-CB and very small amount of 1,4,5,8-tetraaminoanthraquinone dye were filled into the cell gap.

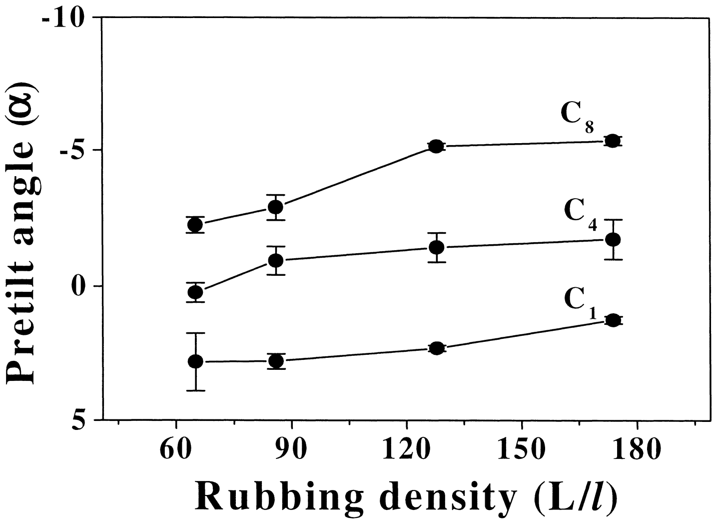

Fig. 4. Pretilt angles of C_m-OPIs.

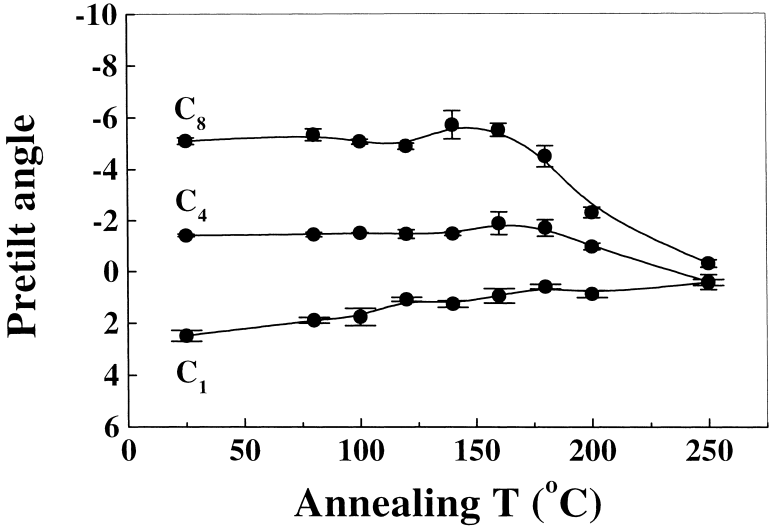

Fig. 5. Pretilt angles of C_m-OPIs at various annealing temperatures.

Pretilt angles were then measured by the crystal rotation method using He-Ne laser beam as a function of rubbing density. In Fig. 4 the pretilt angle values of C_m-OPIs are plotted against the rubbing density. Fig. 4 shows that on the surface of C_1-OPI LC molecules are aligned homogeneously against the rubbing director while C_8-OPI orients 5-CB molecules along the rubbing director and in C_4-OPI the direction of 5-CB alignment changes from parallel to antiparallel depending on rubbing density.

OPI backbones are flexible in their structure, and to examine the effect of the backbone flexibility on LC alignability pretilt angle values were determined for the C_m-OPI samples annealed at various temperatures for 2 h.

Fig. 5 shows that pretilt angles converge to zero with elevating annealing temperature. Although the convergence temperature 250 °C is not identical with the T_g values of the C_m-OPIs, it is to see from Fig. 5 that the backbone rigidity exerts a great effect on the thermal resistance of the rubbing director.

All the other polyimides except C_m-PPIs demonstrated roughly similar LC-aligning and annealing behaviors to C_m-OPIs. C_m-PPIs, which have the most rigid backbone structure,

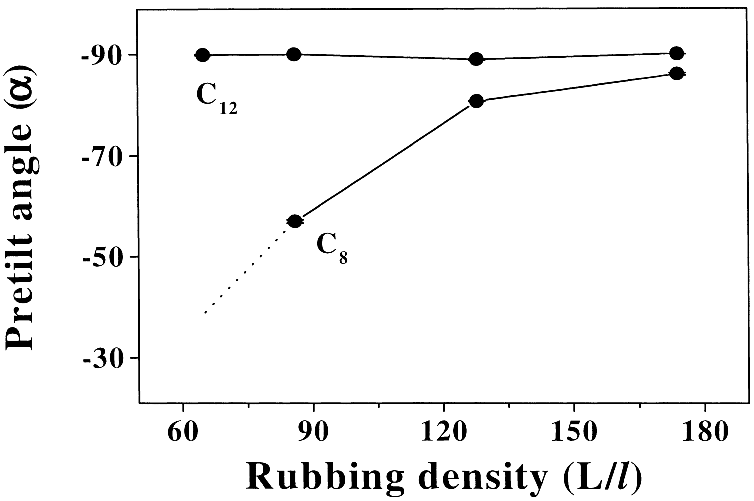

Fig. 6. Pretilt angles of C_m-PPIs.

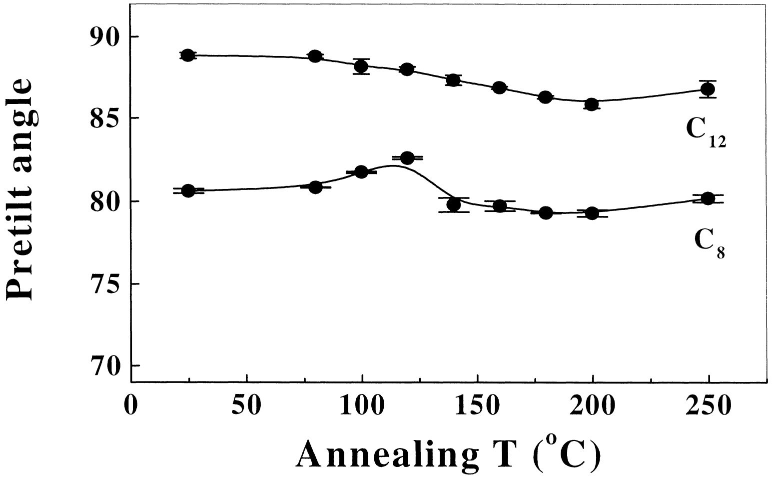

Fig. 7. Effect of annealing on pretilt ange of C_m-PPIs.

show highly unique behavior. As shown in Fig. 6 and Fig. 7, C_{12}-PPI revealed homeotropic LC alignments independent of rubbing density, but in C_8-PPI the LC alignment director changes from homogeneous to homeotropic with increasing rubbing density. This result is highly interesting since the pretilt angle can be controlled by controlling the rubbing density.

In Fig. 7 the effect of annealing on pretilt angles of C_m-PPIs is presented. It shows that the annealing practically does not exert any effect on the disappearance of the pretilt angle at temperatures lower than 250 ^oC. This means again that the rigidity of the polymer backbone strongly affects LC alignability of the polymer structure.

Conclusions

Various novel aromatic polyimides with flexible n-alkyloxy side chains on their dianhydride unit are prepared in film form by condensation of 3,6-di[4-(n-alkyloxy)-phenyloxy]pyromellitic dianhydrides with 7 different commercially available diamines and their properties were measured and discussed with emphasis on backbone structure effect on the LC-aligning properties. From the polyimides prepared C_m-PPIs showed exceptional behavior in solubility, crystallinity, phase transition and LC alignability. This exceptional behavior is assumed to result from their highly rigid backbone structure.

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