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Synthesis and Properties of Fully Aromatic Non-fluorinated Polyimides Exhibiting High Transparency and Low Thermal Expansion

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A fully aromatic unfluorinated polyimide (PI) exhibiting high transparency in the visible region and small thermal expansion was designed and prepared. The formation ability of charge transfer (CT) interactions in PIs estimated using the density functional theory clarified that polychlorine-substituted benzidines should give transparent PIs due to their low electron-donating properties. A combination of 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA) and 2,2',6,6'-tetrachloro-4,4'-diaminobiphenyl (4ClBZ) gave a PI exhibiting good transparency (52% at 420 nm and 81% at 600 nm), a high *T*g (368˚C), a high refractive index (1.6473 at 1.31μm) and a low CTE (13 ppm/K). This material is suitable for thermally stable, transparent, and inexpensive substrates for flexible displays and organic thin film transistors.

Keywords / transparency / aromatic polyimide / low thermal expansion / display applications / density functional theory / density functional theory

1. Introduction

Most of conventional polyimide (PI) films show considerable coloration ranging from pale yellow to deep brown, though the optical transparency of PIs is sometimes of special importance. Rogers first reported that colorless PIs can be synthesized from a dianhydride and a diamine having hexafluoroisopropyridene (–C(CF_3)$_2$–, 6F) groups [1]. Reuter et al. have revealed the potentials of fluorinated PIs as optical waveguide materials [2], and Matsuura et al. reported that fluorinated PIs derived from 2,2'-bis(trifluoromethyl)-4,4'-diaminobiphenyl (TFDB) exhibit high transparency in the visible and near-infrared region as well as low dielectric constants, low refractive indices, and low water absorption, which are suitable for optical applications [3-5]. The coloration of PIs is ascribed to the formation of charge transfer complex (CTC) between alternating electron-donor (diamine) and electron-acceptor (dianhydride) moieties [6]. According to the original CTC formation theory [7], strong electron-donors and strong electron-acceptors stabilize both the ground and the excited state of electrons and reduce the electronic transition energy between occupied and the unoccupied molecular orbitals (MOs). Applying this theory to aromatic PIs, the electronic transition energy from the highest occupied molecular orbital (HOMO) located around the imide-

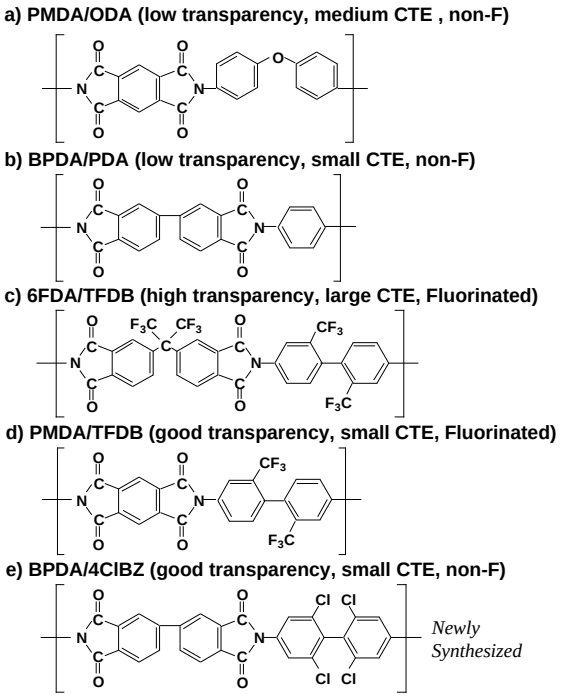

Fig. 1 Structures of representative PIs. The PIs having bent linkages (**a** and **c**) show large CTEs whereas other rigid-rod PIs show small CTEs. However, unfluorinated PIs exhibiting small CTEs and high transparency have never been reported. PI e) proposed in this study is a promising candidate for such demands (see text).

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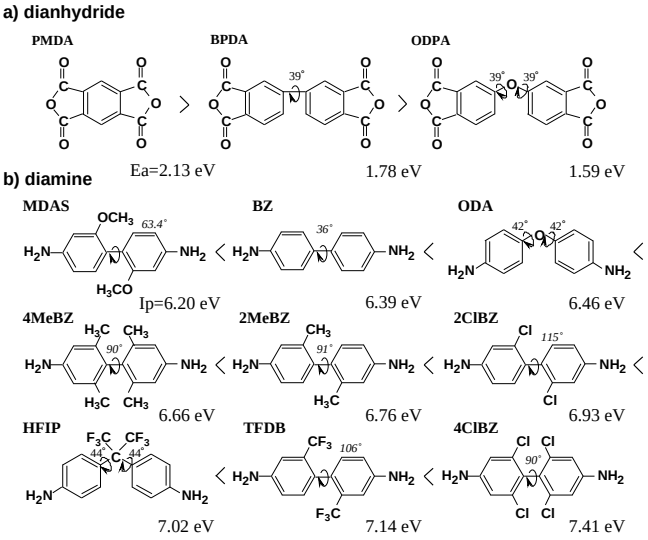
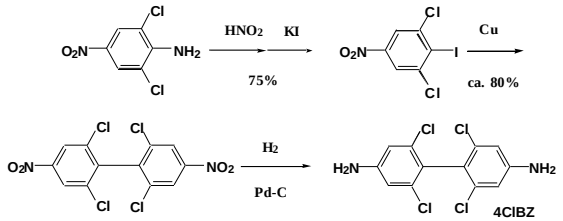


Fig. 1 Strutures of source materials of polyimides. Electron affinities of a) dianhydrides and the ionization potentials of b) diamines were calculated using the DFT theory (B3LYP) with 6-31G* basis set.

nitrogen to the lowest unoccupied molecular orbital (LUMO) located around the carbonyl carbons should be determined from the electron-donating property of diamine and the electron-accepting property of dianhydride. We have reported that the arrangement of the diamine moieties in order of color intensity of polyimides shows fairly good agreement with the order of the electron-donating properties of the diamines estimated from calculated molecular orbital energy of HOMO (ε_{HOMO}) and ^{15}N NMR chemical shifts.[8,9] These results are consistent with the formation of CTC and also indicate that the electron-donating properties of diamines and electron-accepting properties of dianhydrides are retained to a significant extent even in polyimide molecular chains.

We have recently demonstrated that transparent flexible substrates with sputtered ITO (indiumtin oxide) were successfully prepared with a fluorinated PI (6FDA/TFDB), and the substrates can be sufficiently applied to the display devices such as organic electroluminescent displays (OELDs) [10]. The performance of the PI-based device is sufficiently comparable with that of the inorganic glass-based devices and the PI substrate is an excellent candidate for transparent flexible substrates in the display or other electronic applications, especially active matrix type displays or organic thin film transistors (OTFTs). For the display applications, the compatibility of thermal expansion with ITO and/or compound semiconductors is crucial in addition to high transparency in the visible region and high thermal stability. In particular, reduction and control of coefficients of in-plane thermal expansion of PI films is a challenge.



Scheme 1 Synthesis of 4ClBZ.[12]

Furthermore, fluorinated compounds are generally difficult to access due to their high costs. Hence, we aimed to develop novel polyimides having such preferable properties without using fluorinated source materials.

2. Calculation and Measurements

For estimating the electronic properties of source compounds, the density functional theory (DFT) with the three-parameter Becke-style hybrid functional (B3LYP) was adopted, and the 6-311G(d) basis set was used for geometry optimizations under no constraints and the calculation of Ea and Ip. All calculations were performed using Gaussian-03 (Rev.C02) [11] on a Compaq Alpha GS-320.

Ultraviolet-Visible (UV-Vis) absorption spectra of PI films were measured with a Hitachi U-3500 spectrophotometer at room temperature. Thermal mechanical analysis (TMA) was conducted using a Shimadzu TM-5000 analyzer with specimen dimension of 5 x 15 mm and a load of 10g with 10°C/min. Refractive indices were measured with a prism coupler, Metrikon-2000, with home-built apparatus.

3. Materials, Synthesis, and Film Preparation

Pyromellitic dianhydride (PMDA) and 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA) were purchased from Tokyo Kasei Kogyo Co., Ltd. 2,2'-Dichloro-4,4'-diaminobiphenyl (2ClBZ), and 2,2',6,6'-tetrachloro-4,4'-diaminobiphenyl (4ClBZ) were synthesized according to the literature [12]. TFDB was supplied by Central Glass Co., Ltd. Other diamines were purchased from Tokyo Kasei Kogyo Co.,Ltd. All dianhydrides and diamines were purified by sublimation under reduced pressure prior to use. The method of preparing poly(amic acid)s (PAAs) dissolved in *N*,*N*-dimethylacetamide (DMAc) has been described elsewhere [3–5]. The PAA solutions were spin-coated onto 3-inch silicon wafers. After the solvent was removed by drying at 70°C for 1h, the PAA films were heated to 350°C at 4°C/min under nitrogen, kept at 350°C for 1h, and then cooled to room temperature. The thicknesses of the PI films peeled from substrates were measured by a DekTak-3 profilometer. All the films obtained were flexible, tough, and creaseless.

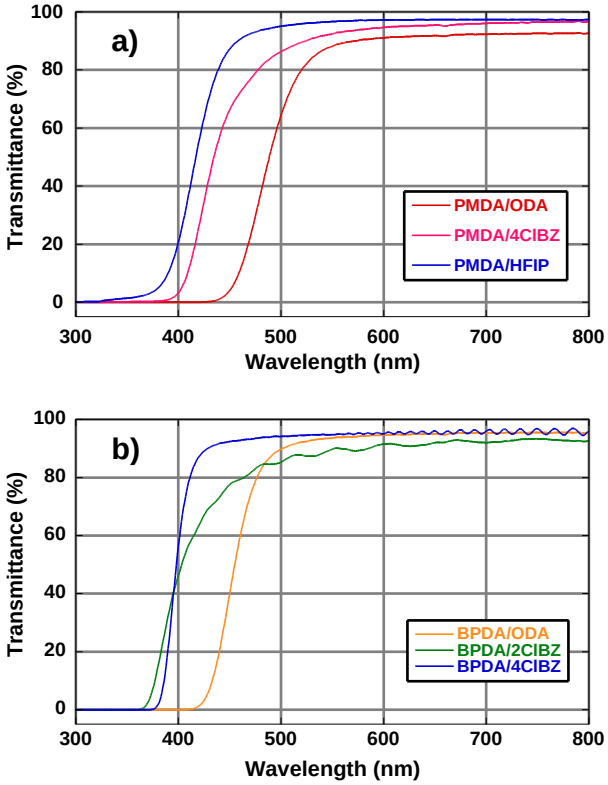


Fig. 2 Optical transmission spectra of PIs derived from a) PMDA and b) BPDA dianhydrides.

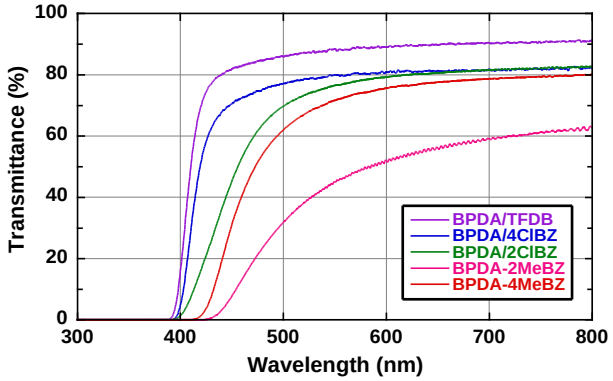


Fig. 3 Optical absorption spectra of PI films derived from BPDA dianhydride. The spectra were obtained for different thickness (11–44 μm), though the transmittance are normalized for 50μm-thick films.

4. Results & Discussion

Figure 2 lists the dianhydrides and diamines used as source materials for PIs in this study together with their most stable conformations (dihedral angles), the calculated electron affinity (Ea) of dianhydrides, and the ionization potentials (Ip) of diamines. Benzidine (BZ) is incorporated as a reference. Since Ea and Ip are proportional to $-\varepsilon_{LUMO}$ and $-\varepsilon_{HOMO}$, they represent the electron accepting properties of dianhydrides and the electron donating properties of diamines, respectively. In addition, ODPA, ODA, and HFIP have bent and flexible ether (–O–) and 6F linkages that should causes significant increases in thermal expansion (CTE). The PIs containing these bent linkages have been reported to exhibit CTEs larger than 30 ppm/K [13]. In contrast, the other structures contain no bent linkages, though the incorporated biphenyl linkages are rotatable. The absence of bent structures shoud be essential to provide low CTEs. Matsuura et al. have reported that PMDA/TFDB shows a small and negative CTE (–0.5 ppm/K) [3]. Although such negative CTE is characteristic to highly orientated rigid-rod aromatic polyamides, namely Kevlar, it is uncommon in uniform films. This phenonenon mainly originates from the very large anisotropy in thermal expansion between the in-plane and the out-of-plane directions of PMDA/TFDB. In addition, it is noteworthy that an unfluorinated 4ClBZ shows the largest Ip in these diamines, suggesting to provide transparent PIs with low CTE and high *T*g due to its rigid-rod structure.

Figure 3 shows the optical transmission spectra of the PI films derived from a) PMDA and b) BPDA dianhyrides with different diamines. The arrangement of the diamine moieties in order of transparency estimated from the wavelengths with transmission=60% [a) HFIP > 4ClBZ > ODA > MDAS, and b) 4ClBZ > 2ClBZ > ODA], agrees well with the order of the electron-donating properties of diamines. Figure 4 also shows the optical transmission spectra of relatively thick films of PIs derived from BPDA. The order of transparency

Table 1 Calculated and measured properties of rigid-rod PIs derived from BPDA dianhydride.

Polyimide	ΔE /eV[a]	*T*g /°C[b]	CTE[c] ppm/K	*d*/μm[d]	color	*T* (%) (estimated for 50μm-thick)[e] 400nm	420nm	600nm
BPDA/TFDB	2.26	321	38	16	pale khaki	16	70	89
BPDA/2ClBZ	2.14	>400(357)	–0.2	44	yellow	1	16	79
BPDA/4ClBZ	2.66	368	13	11	pale khaki	5	52	81
BPDA/2MeBZ	1.95	>400(420)	19	23	yellow	0	0	52
BPDA/4MeBZ	1.90	370[f]	39	32	yellow	0	1	76

[a] Calculated band-gaps ($\varepsilon_{LUMO}-\varepsilon_{HOMO}$) obtained using models, [b] Glass transitiontemperatures determined from TMA, [c] Coefficients of in-plane thermal expansion (80-200°C), [d] Thickness, [e] Transmittance values were estimated assuming 50 μm-thick films. [f] estimated from DSC thermogram.

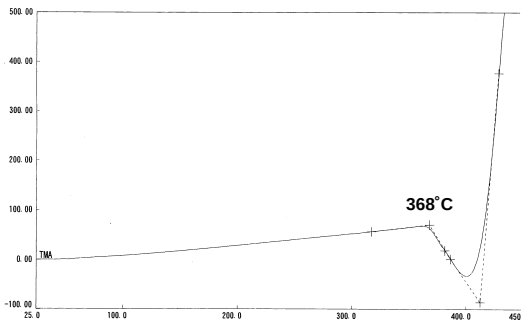


Fig. 4 TMA curve of a 36μm-thick BPDA/4ClBZ PI film. A small CTE of 13 ppm/K was obtained.

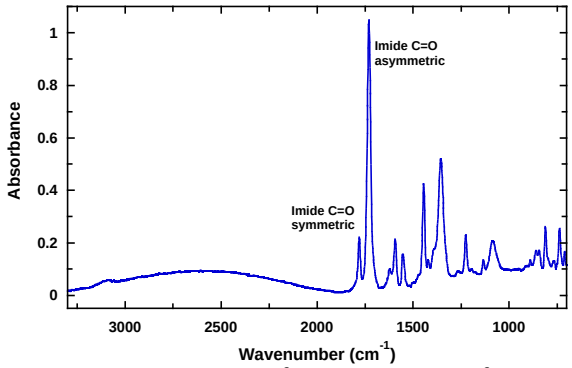


Fig. 5 ATR-IR spectrum of a cross-section of a 90μm-thick BPDA/4ClBZ film, showing complete imidazation.

obtained is HFIP > 4ClBZ > 2ClBZ > 4MeBZ > 2MeBZ. As predicted by DFT calculations, 4ClBZ gives the most transparent PIs in non-fluorinated diamines (though fluorinated PIs derived from HFIP are the most transparent). The reason that HFIP provides highly transparent PIs is ascribable not only to its high Ip (a weak electron donor) but also to the effect of loosening the intermolecular packing due to the low-polarizable and the bulky 6F groups. This effectively prevents the formation of intermolecular CTC. In contrast, although 4ClBZ exhibits a higher Ip than that of HFIP and takes a nonplanar ellipsoidal conformation (ψ=90˚), its polarizability is significantly higher than that of HFIP due to the mobile outer-shell electrons of chlorines. This may promote the intermolecular CTC formation. Table 1 summarizes the properties of PIs derived from BPDA and substituted bendizines. All the PIs show sufficiently high thermal stability (*T*g's over 320˚C), and smaller CTEs than conventional PIs due to their rigid structures. In particular, BPDA/4ClBZ exhibits good transparency (52% at 420 nm and 81% at 600 nm for a 50 μm-thick film), a high *T*g (368˚C), a high refractive index (1.6473@1.31μm) and a low CTE (13 ppm/K from Fig.5) compatible with ITO and semiconductors for flexible substrates for displays. As seen in Fig.5, the BPDA/4ClBZ film abruptly shrank above *T*g, suggesting that the residual stress generated during thermal treatment was released above *T*g, and orientation-induced crystallization might have occurred. The ATR-IR spectrum of a cross-section of this PI (Fig. 6) shows that this PI was fully imidized by thermal curing at 350˚C as evidenced that the symmetric and asymmetric imide C=O stretching vibrations are observed at 1780cm^{-1} and 1730cm^{-1}, respectively, and no peaks for amde acids are observed around 1680cm^{-1}. In addition, this PI exhibits little C–H vibrations at large wavenumbers (around 3000cm^{-1}), which is also suitable for thermally stable, optically transparent, and inexpensive flexible substrates at longer wavelengths such as near-IR.

5. Conclusions

A fully aromatic and unfluorinated polyimide was synthesized from BPDA and 2,2',6,6'-tetrachloro-4,4'-diaminobiphenyl (4ClBZ). The polyimide exhibits good transparency (52% at 420 nmand 81% at 600 nm at 50 μm-thick) in the visible region, high thermal stability (*T*g: 368˚C), and a low CTE (13 ppm/K). This PI also show a higher refractive index (1.6473 at 1.31μm) than conventional PIs. This is promising for inexpensive flexible substrates for organic electroluminescent displays, active matrix type displays, and organic thin film transistors.

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