



# Optically transparent aromatic poly(ester imide)s with low coefficients of thermal expansion (1). Self-orientation behavior during solution casting process and substituent effect



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## ABSTRACT

A series of ester-linked tetracarboxylic dianhydrides were synthesized from trimellitic anhydride chloride and hydroquinone (HQ) analogs including various alkyl substituents. The properties of aromatic poly(ester imide)s (PEsI) prepared from the tetracarboxylic dianhydrides and 2,2'-bis(trifluoromethyl) benzidine (TFMB) were investigated for applications as novel plastic substrate materials in image display devices. The chemically imidized PEsI from trimethyl-substituted HQ was soluble even in less hygroscopic solvents such as cyclopentanone (CPN). Simple casting from the CPN solution provided a flexible and less colored film with a considerably low coefficient of thermal expansion ( $CTE = 11.5 \text{ ppm K}^{-1}$ ), a high  $T_g$  of 276 °C, high thermal stability (5% weight loss temperature in  $N_2$ : 453 °C), and very suppressed water uptake ( $W_A = 0.13\%$ ). The low CTE results from highly aligned main chains along the  $X$ – $Y$  direction, which occurred during solvent evaporation after the PEsI solution was coated on a substrate. A mechanism is also proposed for such self-orientation behavior in this work. On the other hand, the thermally imidized counterpart was worthless in terms of low CTE and high transparency. Some conventional rigid tetracarboxylic dianhydrides were copolymerized with a minor content to di-*tert*-butyl- and diamyl-substituted PEsI systems. This approach was very effective not only for further improving some thermal properties (low CTE and high  $T_g$ ) but also for suppressing film yellowness while keeping excellent solution-processability. Thus, some of the PEsIs developed in this work can be promising candidates as novel plastic substrate materials.

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## 1. Introduction

Optically transparent heat-resistant polymers are indispensable materials for applications to various optoelectronic components, e.g., plastic substrates in image display devices, liquid crystal alignment layers, color filters, optical compensation films, optical fibers, light-guiding plates, and optical lenses. One of the recent important subjects is to replace current fragile inorganic glass substrates (300–700  $\mu\text{m}$  thick) in image display devices by plastic substrates (<50  $\mu\text{m}$  thick), thereby the display panels can become drastically light and flexible. However, no reliable plastic substrate materials are available yet because of difficultness of simultaneously achieving high levels of required properties, i.e., optical transparency, heat resistance, dimensional stability against thermal

cycles in the device fabrication processes (thermal dimensional stability), film flexibility, and film-forming process compatibility (solution-processability). In general, plastic substrates are superior to current inorganic glass substrates in flexibility and thin-film formability but inferior in heat resistance and thermal dimensional stability.

Poly(ether sulfone) (PES) is known to possess the highest  $T_g$  (225 °C) among commercially available super engineering plastics. However, PES is not adapted to the present purpose in terms of short-term heat resistance ( $T_g$ ) and thermal dimensional stability. Plastic substrates with poor thermal dimensional stability undergo significant thermal expansion/contraction during the multiple heating/cooling cycles in the formation processes of indium tin oxide (ITO) electrodes and thin-film transistors, which can be responsible for a serious problem such as an ITO layer breakdown.

The most reliable high-temperature polymeric materials are polyimides (PI) [1–4]. Some of aromatic PI systems also possess excellent thermal dimensional stability based on the combination

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of their much higher  $T_g$  than the device processing temperatures and the low linear coefficients of thermal expansion (CTE) along the film plane ( $X$ – $Y$ ) direction in the glassy region. However, conventional aromatic PIs show intensive coloration arising from charge-transfer (CT) interactions [5], which often disturbs their optical applications. The coloration/decoloration mechanism of aromatic PI films has been so far extensively studied from fundamental and industrial interests [5]. One of the effective approaches for the decoloration is to inhibit CT interactions by choosing non-aromatic (cycloaliphatic) monomers either in diamines or tetracarboxylic dianhydrides or both [6–16]. However, the use of cycloaliphatic monomers causes some serious problems; semi- or wholly cycloaliphatic PI films often possess poor thermal dimensional stability based on their high CTE values ( $>60$  ppm  $K^{-1}$ ) in the glassy region, even if their  $T_g$ 's were very high ( $>300$  °C). Such high CTE arises from practically three-dimensionally random chain orientation. Most of cycloaliphatic monomers consist of non-linear/non-planar steric structures [8,9]. As a result, the overall main PI chain linearity is completely destroyed. Such distorted backbone structures do not give rise to high extents of chain alignment along the  $X$ – $Y$  direction (called “in-plane orientation”) upon thermal imidization process [13,14,17]. Among cycloaliphatic monomers, 1,2,3,4-cyclobutanetetracarboxylic dianhydride (CBDA) and *trans*-1,4-cyclohexanediamine (*t*-CHDA) are rare cases with stiff/linear structures. However, once these monomers were used, the resulting PIs lose solution-processability. On the other hand, a wholly aromatic PI system derived from 4,4'-(hexafluoroisopropylidene) diphthalic anhydride (6FDA) and 2,2'-bis(trifluoromethyl)benzidine (TFMB) is known as a very limited case with high transparency and good solubility, although this PI film owns no low CTE characteristics, [18,19] on the basis of a non-linear/non-coplanar steric structure of the 6FDA-based diimide unit [20]. Thus, the current situation suggests how it is difficult to develop reliable plastic substrate materials with the multiple target properties.

We have previously challenged to develop solution-processable low-CTE transparent PI systems without using any cycloaliphatic monomers and reported that the combination of an amide-linked tetracarboxylic dianhydride including trifluoromethyl ( $CF_3$ ) groups and TFMB led to excellent combined properties applicable to the plastic substrate materials [19]. The results motivated us to accomplish the target properties by using novel lower-cost aromatic tetracarboxylic dianhydrides without  $CF_3$  groups, which can be prepared via a much simpler process as described later. The present work highlights aromatic poly(ester imide)s (PEIs) as the key materials. We have so far studied low-CTE PEIs with suppressed water absorption for applications as higher-performance dielectric substrates in flexible printed circuit boards (FPC) [21–23]. In this case, the PI film transparency was not a great matter of concern for FPC applications. However, we happened to be aware that the coloration of the PEI films was appreciably weaker than that of conventional aromatic PIs and amide-containing PIs [19,21]. This observation gave us an idea; an elaborate chemical modification of the PEIs may produce promising less colored high-temperature plastic substrate materials. The present work proposes a series of PEIs modified by introducing various alkyl groups and discusses a substituent effect on the target properties.

## 2. Experimental

### 2.1. Materials

#### 2.1.1. Monomer synthesis

Ester-linked tetracarboxylic dianhydrides were synthesized from various hydroquinone analogs (HQs) and trimellitic anhydride

chloride (TMAC) in the presence of pyridine as an HCl acceptor in anhydrous tetrahydrofuran (THF) as described in our previous work [19], recrystallized from suitable solvents, and dried at 160 °C in vacuum for 12 h. The products were characterized by FT-IR and  $^1H$  NMR spectroscopy, elemental analysis, and differential scanning calorimetry (DSC). As a typical example, the analytical results for the product from TMAC and 2,5-di-*tert*-butylhydroquinone (25DBHQ, Fig. 1) are as follows; melting point: 325 °C (endothermic peak), FT-IR (Jasco, FT/IR 4100, KBr,  $cm^{-1}$ ): 3059 ( $C_{arom-H}$ ), 2959 ( $C_{aliph-H}$ ), 1871/1780 (acid anhydride  $C=O$ ), 1748 (ester  $C=O$ ), 1487 (1,4-phenylene unit),  $^1H$  NMR [Jeol, JNM-ECP400, 400 MHz, dimethyl sulfoxide ( $DMSO$ )- $d_6$ ,  $\delta$ , ppm]: 8.70 [d, 2H,  $J = 8.0$  Hz, 6,6'-protons of phthalic anhydride (PA)], 8.61 (s, 2H, 3,3'-protons of PA), 8.33 (d, 2H,  $J = 8.0$  Hz, 5,5'-protons of PA), 7.41 (s, 2H, central disubstituted phenylene), 1.30 (s, 18H, *tert*-butyl group). Anal. Calcd (%) for  $C_{32}H_{26}O_{10}$  (570.54): C, 67.36; H, 4.59. Found: C, 67.19; H, 4.59. An analog from trimethyl-substituted HQ (TMHQ, Fig. 1) was also synthesized and characterized in a similar manner; FT-IR (KBr,  $cm^{-1}$ ): 3109 ( $C_{arom-H}$ ), 2933 ( $C_{aliph-H}$ ), (1857/1782 (acid anhydride  $C=O$ ), 1735 (ester  $C=O$ ), 1480 (1,4-phenylene unit),  $^1H$  NMR ( $DMSO$ - $d_6$ ,  $\delta$ , ppm): 8.76–8.65 (m, 4H, 3,3',6,6'-protons of PA), 8.33–8.30 (m, 2H, 5,5'-protons of PA), 7.23 (s, 1H, central tri-substituted phenylene), 2.16–2.09 (m, 9H,  $CH_3$ ). Anal. Calcd (%) for  $C_{27}H_{16}O_{10}$  (500.41): C, 64.80; H, 3.22. Found: C, 64.64; H, 3.27. Other relevant monomers were also synthesized in a similar manner. In this work, the ester-containing tetracarboxylic dianhydrides were designated as TA-X ( $X =$  hydroquinone analogs), e.g., “TA-TMHQ” in case of  $X =$  trimethylhydroquinone (TMHQ).

#### 2.1.2. Polyaddition, imidization, and film preparation

The sources, purification methods, and melting points of monomers and raw materials are summarized in Supplementary data 1. PEI precursors [poly(amic acid)s (PAA)] were prepared by equimolar polyaddition of tetracarboxylic dianhydrides and diamines in dry *N,N*-dimethylacetamide (DMAc) as described in our previous papers [13–16,19]. The reaction scheme is shown in Fig. 2. The formation of PAAs was confirmed from the transmission-mode FT-IR spectra recorded on an FT/IR 4100 infrared spectrometer (Jasco) using separately prepared thin cast films (4–6  $\mu m$  thick) with a non-uniform thickness to erase interference fringes. A typical FT-IR spectrum is depicted in Fig. 3(a). Some specific bands ( $cm^{-1}$ ) are observed: 3259 (amide,  $N-H$ ), 3057 ( $C_{arom-H}$ ), 2969/2878 ( $C_{aliph-H}$ ), 2630 (hydrogen-bonded  $COOH$ ,  $O-H$ ), 1735 (ester,  $C=O$ ), 1687/1534 (amide,  $C=O$ ), 1490 (1,4-phenylene unit), and 1323 ( $CF_3$ ,  $C-F$ ).

The PAAs were converted to PEIs by different methods (thermal and chemical imidization) (Fig. 2). When the imidized forms were highly soluble, PAAs were chemically imidized as previously described [14,16,19]. The imidized samples isolated as fibrous white precipitates were re-dissolved in a fresh anhydrous solvent [e.g., cyclopentanone (CPN), triglyme (Tri-GL), or DMAc] at a solid content of 5–15 wt%. The homogeneous PEI solutions were coated on a glass substrate and dried typically at 60 °C for 2 h in an air convection oven and successively heated typically at 250 °C for 1 h in vacuum on the substrate. After peeling them off from the substrate, the PEI films (typically 20  $\mu m$  thick) were annealed typically at 255 °C/1 h in vacuum to remove residual stress. The thermal conditions were properly adjusted for obtaining better quality of films. The samples prepared via chemical imidization are denoted as “(C)” from now on.

PEI films were also prepared upon thermal imidization; PAA solution was bar-coated on a glass substrate, dried at 60 °C for 2 h in an air-convection oven, and heated typically at 200 °C/0.5 h + 350 °C/1 h in vacuum on the substrate, and successively annealed in vacuum at 10–20 °C lower temperatures than the  $T_g$

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