

Heat-resistant Wholly Aromatic Poly(ester imide)s with Low Thermal Expansion Properties, Optical Transparency, and Solution-Processability

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Abstract: This study proposes wholly aromatic poly(ester imide)s (PEIs), which are promising candidates as novel plastic substrate materials for use in image display devices. A series of ester-linked tetracarboxylic dianhydrides (TA-X) were synthesized from trimellitic anhydride chloride (TMAC) and 4,4'-biphenol analogs containing different numbers and positions of methyl substituents and they were combined with 2,2'-bis(trifluoromethyl)benzidine (TFMB). A significant substituent effect on the target properties [T_g , optical transparency, and the linear coefficient of thermal expansion (CTE), and ductility] was observed. A chemically imidized PEI containing 2,2',3,3',5,5'-hexamethyl-substituted *p*-biphenylene unit was highly soluble at room temperature, even in less hygroscopic non-amide solvents such as cyclopentanone (CPN). The CPN-cast PEI film was almost colorless, as suggested from the rather low yellowness index (YI = 3.2), high light transmittance at 400 nm ($T_{400} = 71.5\%$), and very low haze (1.15%). This PEI film also possessed a high T_g (294 °C) in addition to a low CTE (21.7 ppm K⁻¹), moderate film ductility, and very low water uptake. This PEI was modified by copolymerization with another rigid tetracarboxylic dianhydride for further reducing the CTE while maintaining the other excellent target properties.

Keywords: Aromatic Poly(ester imide); Optical Transparency; Linear Coefficient of Thermal Expansion (CTE); Solution Processability; Self-orientation; Heat-resistant Plastic Substrate

1. INTRODUCTION

Colorless heat-resistant polymers are key materials for recent widespread optical and optoelectronic applications. Optically transparent plastic substrate materials with excellent heat resistance are indispensable for dramatic weight saving and improvements in bendability and impact resistance for image display devices. However, reliable heat-resistant plastic substrates are not available yet because of the great difficulty in simultaneously

Ester-linked Tetracarboxylic Dianhydrides

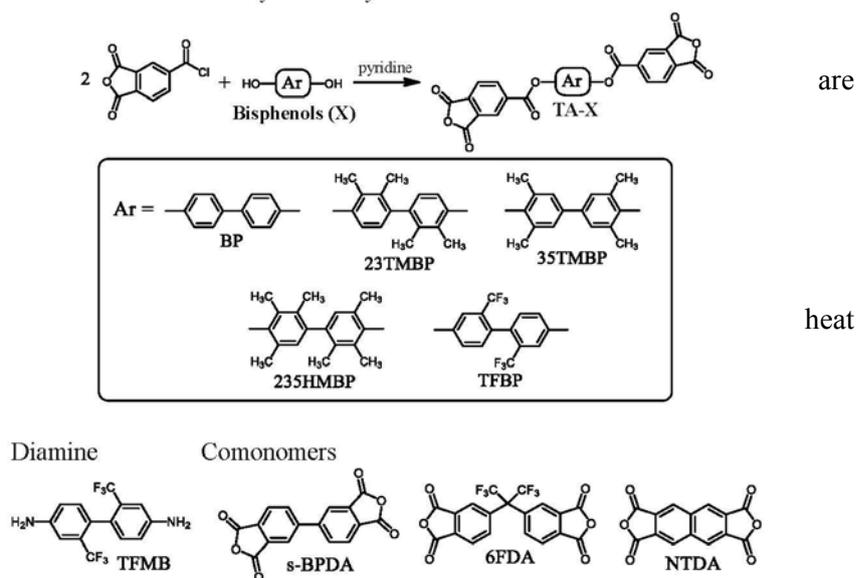


Fig.1 Reaction scheme for the synthesis of ester-linked tetracarboxylic dianhydrides and the structures of the other

achieving the required properties, i.e., optical transparency, heat resistance, dimensional stability against

thermal cycles during device fabrication, film flexibility, and simple film processability. Even poly(ether sulfone) (PES), which has the highest T_g (225 °C) among conventional transparent super engineering plastics, is not suitable in terms of short-term heat resistance (T_g) and CTE as the key index of thermal dimensional stability.

On the other hand, some of wholly aromatic polyimide (PI) films can overcome these serious thermal problems. However, conventional aromatic PI films usually have intensive coloration arising from charge-transfer (CT) interactions [1], which often disturb their optical applications. Therefore, optically transparent (colorless) PIs and other high-temperature polymers have been widely studied [2]. However, in fact, colorless wholly aromatic PIs are almost limited to a PI system derived from 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (6FDA) and TFMB. This PI also has a high T_g (327 °C) and excellent solubility, whereas it shows no low-CTE property, owing to its distorted main chain structure.

The most effective approach for the decoloration of PI films is to inhibit the CT interactions by choosing non-aromatic (cycloaliphatic) monomers, either diamines or tetracarboxylic dianhydrides or both [1]. However, in PIs containing cycloaliphatic units, there is a concern regarding the durability for the target properties during device fabrication and long-term use of device, although the durability of PIs containing cycloaliphatic units is not yet fully understood.

As a potential strategy for achieving the above-mentioned target properties without using cycloaliphatic monomers, we have studied a series of soluble aromatic PEIs containing various substituents [3]. In particular, when an ester-linked tetracarboxylic dianhydride (TA-TMHQ) derived from 2,3,5-trimethylhydroquinone and TMAC was combined with TFMB, the solution-cast PEI film prepared via chemical imidization displayed excellent combined properties: a relatively high transparency ($T_{400} = 65\%$), a very low CTE (12 ppm K^{-1}), a relatively high T_g [276 °C by thermo-mechanical analysis (TMA)], sufficient ductility, and good solution-processability [3]. Thus, there was room for further improving the T_g and transparency. However, the enhancement of T_g without the deterioration of other target properties is a challenging subject because molecular designs toward the enhancement of T_g causes negative influences: a decrease in solubility (consequently, disappearance of chemical imidization process compatibility) and often, film coloration. In this report, we propose PEIs containing alkyl-substituted *p*-biphenylene units for this purpose [4].

2. EXPERIMENTAL

A series of ester-linked tetracarboxylic dianhydrides were synthesized from various alkyl-substituted 4,4'-biphenols and TMAC according to the reaction scheme shown in **Fig.1** and sufficiently purified by recrystallization. The structures were confirmed by FT-IR, 1H -NMR, elemental analysis, and DSC.

PI precursors [poly(amic acid)s (PAAs)] were prepared via equimolar polyaddition between tetracarboxylic dianhydrides and diamines in DMAc at room temperature. After the PAA solutions were adequately diluted with DMAc, chemical imidization was carried out by slowly adding a dehydrating agent [acetic anhydride (Ac_2O)/pyridine (7/3, v/v)] to PAA solutions at a fixed molar ratio of $[Ac_2O]/[COOH]_{PAA} = 5$ with continuous vigorous stirring and successive stirring at room temperature for 12 h in a sealed bottle. After the reaction mixture was adequately diluted, the reaction mixture was very slowly poured into a large amount of methanol/water to form fibrous white precipitate.

The $^1\text{H-NMR}$ spectra of the PI powder samples in $\text{DMSO-}d_6$ indicated that the chemical imidization process provided practically fully imidized PEIs for most of the systems examined in this study, which was confirmed by the complete disappearance of the amide proton signal at $\delta \sim 10$ ppm. The progress of polymerization was confirmed by GPC and inherent viscosity measurements. The chemically imidized PI powder was dissolved in a fresh anhydrous solvent [CPN, γ -butyrolactone (GBL), triglyme (TriGL) or DMAc] at a solid content of 8–15 wt.%. The homogeneous PEI solutions were coated on a glass substrate, and dried for 2 h at 60 °C for CPN and DMAc as the solvents, 80 °C for GBL, 100 °C for TriGL in an air convection oven, followed by at 250 °C for 1 h under vacuum on the substrate. After being peeling off from the substrate, the PEI films (typically 20 μm thick) were annealed at 250 °C for 1 h under vacuum to remove residual stress. The thermal conditions were optimized to obtain better quality films.

In this work, the following target properties of PEI films were evaluated: the optical properties (T_{400} , the total light transmittance (T_{tot}), haze, yellowness index (YI), birefringence (Δn_{th}), thermal properties (T_g , CTE, and the 5% weight loss temperatures (T_d^5) in N_2 and air atmosphere, tensile properties [tensile modulus (E), tensile strength (σ_b), and the elongation at break (ϵ_b)], and water uptake (W_A).

3. RESULTS AND DISCUSSION

We have revealed that the effect of the film preparation route on the film properties is very significant. PI films prepared via chemical imidization always exhibited higher optical transparency and lower CTE values than those prepared via the conventional two-step process (*i.e.*, precursor casting and successive thermal imidization) [2]. These results suggest that compatibility with the chemical imidization process (namely, excellent solubility of the imidized form for avoiding gelation and precipitation during chemical imidization) is the key for achieving our goal.

In the PEI system derived from non-substituted TA-BP (**Fig.1**) and TFMB, gelation occurred during chemical imidization because of its poor solubility. Therefore, the PEI film (#1) was prepared via thermal imidization of the PAA cast film (two-step process). This PEI showed a relatively low CTE (32.9 ppm K^{-1}) and a very high T_g (340 °C). However, the film was significantly colored.

On the other hand, the PEI system (#2) derived from TFMB and TA-23TMBP (**Fig.1**) with four methyl substituents possessed dramatically improved solubility, consequently, chemical imidization process became compatible. This is probably attributed to disturbed closer chain stacking based on the presence of the 2,2',3,3'-substituted bulky methyl groups on the biphenylene unit, which also cause a highly distorted conformation of the biphenylene unit. A feature was observed for the properties of the CPN-cast PEI film (#2) prepared via chemical imidization; *i.e.*, a significantly reduced CTE (15.5 ppm K^{-1}) and an unexpectedly decreased T_g (215 °C).

The use of TA-35TMBP with four methyl substituents at different positions caused an increase in the T_g (261 °C) and a somewhat increased CTE (26.7 ppm K^{-1}) compared to those of the TA-23TMBP/TFMB system. However, the CPN-cast TA-35TMBP/TFMB film (#3) was hazy (haze = 7.3%). Thus, as long as TA-23TMBP and TA-35TMBP are used, it was difficult to enhance the T_g while maintaining a low CTE, low coloration, and low turbidity.

Then, we investigated another PEI system derived from TFMB and 2,2',3,3',5,5'-hexamethyl-substituted TA-235HMBP, which consists of a structurally combined form between TA-23TMBP and TA-35TMBP in terms of the position and number of methyl substituents. The film properties of the TA-235HMBP/TFMB

system (#4) are summarized in **Table 1**. The chemically imidized powder sample was highly soluble in various common organic solvents including less hygroscopic solvents [CPN, GBL, TriGL, and chloroform (CF)]. The CPN-cast PEI film (#4) was almost colorless, as indicated from its rather low YI (3.2), high T_{400} (71.5%), and very low haze (1.15%). Our main intention in this study (to enhance the T_g while maintaining the other target properties) was successful; the PEI system (#4) displayed an enhanced T_g (294 °C by TMA) compared to that of the TA-TMHQ/TFMB system (276 °C by TMA [3]), in addition to a low CTE (21.7 ppm K^{-1}), moderate film ductility ($\epsilon_b^{\max} = 20\%$), and an extremely low W_A value (0.04%).

Structural modifications were carried out by copolymerization with s-BPDA (30 mol%) into the TA-235HMBP/TFMB system. The partial use of s-BPDA (#5) did not cause a significant decrease in the solubility. Except for a slight increase in the T_g , no appreciable property improvement was observed by this approach. On the other hand, copolymerization with NTDA (30 mol%, #6) was effective in reducing the CTE (11.5 ppm) while maintaining other excellent properties, as shown in **Table 1**.

Table 1 Properties of PEI films prepared via chemical imidization for PEIs derived from TFMB with hexamethyl-substituted TA-BPs and related copolymers.

No.	Tetracarboxylic dianhydride	η_{inh} (PEI) ($dL\ g^{-1}$)	T_{400} (%)	YI	Haze (%)	T_g (°C)	CTE (ppm/K)	E (GPa)	σ_b (GPa)	$\epsilon_b^{av/max}$ (%)
4	TA-235HMBP	3.16	71.5	3.2	1.15	294	21.7	4.50	0.19	11/20
5	TA-235HMBP(70) s-BPDA(30)	2.96	62.3	3.4	1.24	298	22.5	4.55	0.19	11/18
6	TA-235HMBP(70) NTDA(30)	2.14	70.2	3.3	1.90	284	11.5	4.99	0.14	5/6

Fig.2 shows performance balance for the TA-235HMBP/TFMB system (#4) and other related systems. When the spider charts are more equally and largely expanded, it represents that the materials possess a good performance balance. The spider charts for the target properties were prepared on the basis of five-ranked criteria listed in **Table 2** [4]. Thermally imidized CBDA/TFMB system [**Fig.2(b)**] has a high T_g and high transparency, however, there was a poor extension of the chart to the left, owing to the poor solution-processability and the insufficient film toughness. The chemically imidized 6FDA/TFMB system seems almost to fulfill the target properties, except for low CTE property, as shown in **Fig.2(c)**. In contrast, the thermally imidized PMDA/TFMB system [**Fig.2(d)**] scores well regarding its low-CTE and high- T_g properties, but, the other required properties are insufficient. Thus, it is not easy to maintain excellent performance balance. On

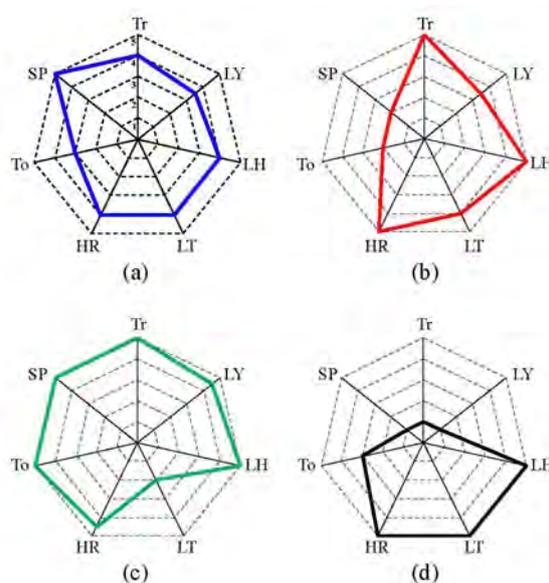


Fig.2 Performance balance based on five-rank evaluation for some TFMB-based systems: (a) TA-235HMBP/TFMB, (b) CBDA/TFMB, (c) 6FDA/TFMB, and (d) PMDA/TFMB.

the other hand, the TA-235HMBP/TFMB system (#4) displayed a relatively uniformly extended spider chart, as shown in **Fig.2(a)**. The results suggest that this PEI system is a promising candidate as novel plastic substrate materials for use in image display devices.

Table 2 Criteria for five-rank evaluation of the target properties.

Properties	Parameters	Relative rank				
		1	2	3	4	5
Light transmittance (Tr)	T_{400} (%)	< 5	20–30	40–60	70–75	> 80
Low yellowness (LY)	YI	> 20	7–10	4–6	2–3	< 1
Low haze (LH)	Haze (%)	> 5	4–3	3–2	2–1	< 1
Low thermal expansion property (LT)	CTE (ppm K ⁻¹)	> 70	60–50	45–35	30–20	< 10
Heat resistance (HR)	T_g (°C)	< 200	220–240	250–270	280–300	> 350
Toughness (To)	ϵ_b^{\max} (%)	No film-forming ability or < 2	5–10	20–30	40–60	> 100
Solution-processability (SP)	Qualitative solubility	Insoluble upon heating	Partially soluble or swelled	Soluble in hot amide solvents	Soluble in amide solvents at r.t. or hot ether solvents	Soluble in various non-amide solvents at r.t.

SP-rank = 3.5 for samples soluble in hot CPN or hot GBL; SP-rank = 1 or 2 for systems without CI process compatibility.

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