

Poly(ester imide)s as Dielectric Substrates in FPC, their Dimensional Stability, Mechanical Properties, and Non-flammability

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Abstract: Some commercially available polyimide (PI) films are known to possess good dimensional stability against various thermal processes, which is based on their low linear coefficients of thermal expansion (CTE). Therefore, they are used as dielectric substrates (base films) in flexible printed circuit boards (FPC). However, the dimensional stability against water/moisture absorption is not always sufficient for the current PI systems. In the present work, we propose poly(ester imide)s (PEIs) as a new type of the base film materials. The PEI films simultaneously achieved low CTE comparable to that of copper foils, suppressed water absorption (W_A), low linear coefficients of humidity expansion (CHE), very high glass transition temperatures (T_g), sufficient film toughness. An increase in the content of the ester groups incorporated in the PI main chains somewhat reduced the non-flammability. In order to solve this problem, we prepared novel phosphorus-containing monomers. Copolymerization using the P-containing monomers at a minor content drastically improved the non-flammability while maintaining the excellent combined properties. Recently, easily foldable low-stiffness FPCs are desired in some cases. The use of lower-modulus base films can be an effective strategy for this purpose. The present work also discusses an approach addressed to lower modulus without sacrificing excellent combined properties.

1. Introduction

Polyimides (PIs) have been widely utilized in a variety of micro- and optoelectronic applications, for example, as the base films for flexible printed circuit boards (FPC) and the tape-automated bonding (TAB), the chip-on-film (COF) assembly systems, the buffer coat films and interlayer dielectrics for LSI chips, high temperature adhesives, light waveguides for their combined excellent properties, i.e., high glass transition temperature (T_g), high resistance to chemicals and radiation, relatively low dielectric constants, and good mechanical properties [1]. The present article describes novel high-temperature dielectric materials useful for the base films of the copper clad laminates (CCL), from which FPC, TAB, and COF are fabricated. Adhesive-free CCL has an advantage from the viewpoints of the CCL dimensional stability against some heat cycles during the circuit board fabrication processes, compared to that using thermally less stable conventional adhesives. The former (two-layered CCL) is usually produced by thermal imidization after solution-casting of PI precursors, poly(amic acid)s (PAAs) onto a copper foil or a metalizing technique consisting of the Cu-plating process after the formation of a Ni-Cr sputtered seed layer.

Thermal dimensional stability of the PI films themselves is also one of the key properties for higher-density assembly using higher performance CCLs. For this purpose, lowering the CTE of the PI films is one of the most effective approaches. The low CTE characteristics of PI base films are also important for obtaining completely flat two-layered CCLs through the casting method. In this case, the

CTE of the base films must be precisely controlled to practically the same value as that of the copper layer (18 ppm/K), otherwise the CCL undergoes curling. Previous reports revealed that low CTE is closely correlated to the extents of chain alignment parallel to the film plane, often called "in-plane orientation" [2,3]. It should be noted that simple solution casting of common polymer systems onto a substrate usually causes no significant in-plane orientation, consequently, no low CTE characteristics. This means that in some low-CTE PI systems a sort of "self-orientation" occurs during the thermal imidization process of the PAA films cast onto substrates under some restricted structural and processing conditions [3 - 6]. We have previously proposed a hypothesis for its mechanism where their stiff/linear backbone structures play a great role for a liquid crystal-like interaction for the self-orientation phenomenon, as a result, lower CTE generation [3].

Another important key property for higher-performance CCLs is the dimensional stability against absorbed water/moisture. It is effective to reduce the linear coefficients of humidity expansion (CHE) of the base films themselves. A primary strategy for decreasing CHE is to suppress the extents of water absorption (W_A) in the PI resins as much as possible. Conventional PIs such as the PMDA/4,4'-ODA system (PMDA = pyromellitic dianhydride, 4,4'-ODA = 4,4'-oxydianiline) tend to absorb well water/moisture compared to polyesters such as poly(ethylene terephthalate). This originates from a high content of highly polarized imide groups in the PMDA/4,4'-ODA structure. Recently we proposed a sort of hybrid material between PIs and polyesters, namely, poly(ester imide)s (PEIs) as a new CCL base film material with significantly decreased water absorption [7 - 9].

In contrast to our PEI systems, most of previously reported PEIs were prepared via the direct polycondensation from imide-containing diols with dicarboxylic acids without the pathway of thermal imidization. Because of poor solubility of the directly polycondensed PEIs, there are very limited reports on the properties of their casing films. Instead, they have been so far studied only in the limited viewpoints of basic properties such as thermal stability, solvent solubility, and mechanical properties [10-16], tensile properties of fibers [17], liquid crystallinity [18 - 20] without any attentions toward CCL applications. A prominent feature of our PEI systems is that the PEI films can be directly formed on copper substrates without any adhesives via the conventional two step processes, i.e., thermal imidization after solution-casting of highly soluble PEI precursors like as conventional PI systems.

We undertook the studies on PEIs as novel CCL base film materials from some simple systems, namely, PEIs derived from an ester-containing tetracarboxylic dianhydride, hydroquinone bis(trimellitate anhydride) (TAHQ) with an ester-containing diamines,

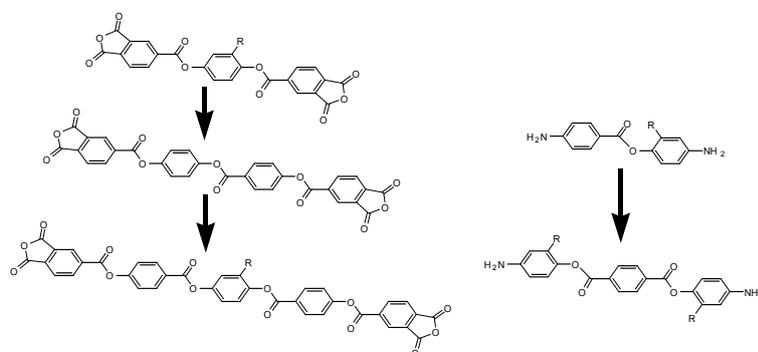


Figure 1. Changes in our key monomers addressed to 4-aminophenyl-4'-aminobenzoate (APAB) and/or 4-amino-2-methylphenyl-4'-aminobenzoate (M-APAB). For these systems, copolymerization using a minor fraction of flexible 4,4'-ODA led to

good combined properties, i.e., a very low W_A , a low CTE comparable to that of copper foil, and sufficient film toughness at the same time [7,8]. Our recent approach is to extend the para-aromatic ester linkages in the monomer structures. Our ester-containing monomers have been going through as shown in **Figure 1**. However, another problem was actualized in this approach; a trend of a decrease in non-flammability with extension of the aromatic ester linkages in the monomer structures. As another approach, we also synthesized some unique tetracarboxylic dianhydrides incorporating biphenylene, *p*-terphenylene, and *p*-quarterphenylene units via ester linkages. The results will be reported elsewhere.

In the present work, we discuss the effects of substituents and the extended aromatic ester linkages on the target properties (CTE, CHE, T_g , and toughness, etc.) together with the structure–non-flammability relationship in our PEI systems. An effect of a phosphorus-containing tetracarboxylic dianhydride on non-flammability is also briefly mentioned in this work.

2. Experimental

2.1 Monomer synthesis

Figure 2 shows a reaction pathway for ester-containing tetracarboxylic dianhydrides used in the present work. 4-Acetoxybenzoyl chloride (AcBC, 200 mmol), derived from 4-hydroxybenzoic acid, was reacted with diols (100 mmol), i.e., hydroquinone (HQ), methylhydroquinone (M-HQ), and 4,4'-biphenol (4,4'-BP) in the presence of pyridine as a HCl acceptor to form diacetates. The use of an ammonia aqueous solution allowed hydrolysis of the terminal acetoxy groups without hydrolysis of the central ester groups. Ester-containing tetracarboxylic dianhydrides were obtained by the reaction of the diols obtained (50 mmol) and trimellitic anhydride chloride (TMAC, 100 mmol) in the presence of pyridine. The products obtained were purified by repeated recrystallization from suitable solvents.

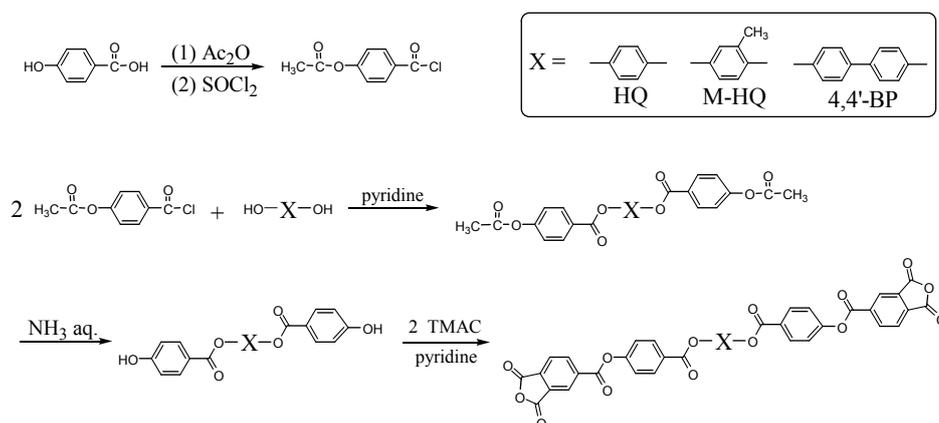


Figure 2. Synthetic route of ester-containing tetracarboxylic dianhydrides used in

The molecular structures of the products were confirmed by FT-IR, $^1\text{H-NMR}$ spectroscopy, and the elemental analysis. All the products showed a very sharp endothermic peak at each melting point in the DSC thermograms, indicating their considerably high purity suitable for PAA polymerization. In this article, these ester-containing tetracarboxylic dianhydrides prepared using HQ, M-HQ, and

4,4'-BP as starting materials are abbreviated as TAHQHB, TAMPHB, and TA44BPHB, respectively.

2.2 Polymerization and film preparation upon thermal imidization

PEsI precursors, poly(ester amic acid)s (PEsAAs), were prepared as follows: tetracarboxylic dianhydride powder (5 mmol) was added into a *N*-methyl-2-pyrrolidone (NMP) solution of diamines (5 mmol) with continuous stirring at room temperature for a prolonged period until the reaction mixture turned to a viscous/homogeneous solution and the solution viscosities were stabilized.

The PEsAA solutions were coated on a glass substrate and dried at 80 °C for 3 h in an air-convection oven. The PEsAA films obtained were thermally imidized as fixed on a glass substrate at established temperatures (typically 250 °C/1 h + 300 °C/1 h) in vacuum. The PEsI films obtained were removed from the substrate and successively annealed at an established temperature (typically at 350 °C/1 h) in vacuum to eliminate residual stress. Complete thermal transformation from PEsAA to PEsI was confirmed from the disappearance of amide C=O (1657, and 1556 cm⁻¹) and hydrogen bonded OH stretching bands (in COOH, around 2600 cm⁻¹) and the appearance of the imide specific bands [1781, 1725 (imide + ester), 1367, 721 cm⁻¹]. There were no appreciable changes in the FT-IR spectra between the imidized sample at 250 °C and the annealed samples at 300–400 °C, suggesting that PEsIs are thermally stable against any side reactions such as transesterification. No indication of thermal crosslinking in the DMA curves, which is suggested from an increase in the storage modulus above the glass transition temperatures, was also observed for all PEsI films.

2.3 Measurements

The reduced viscosities of PEsAAs were measured at 0.5 wt% in NMP at 30 °C using an Ostwald viscometer. The reduced viscosity can be practically regarded as inherent viscosity ($[\eta]_{\text{PAA}}$).

The CTEs of PEsI films (20 mm long, 5 mm wide, and typically 15 μm thick) were measured at a heating rate of 5 °C/min as an average within 100–200 °C for the film plane direction on a thermomechanical analyzer (Bruker-AXS TMA 4000) with a constant load (0.5 g per film thickness in μm) in a nitrogen atmosphere. In this case, the data were collected from the second heating run with a continuous dry nitrogen flow after pre-heating up to 120 °C to eliminate the adsorbed water since the first run occasionally shows an abnormal TMA curve.

Dimensional changes of the PEsI specimens were also monitored at fixed temperature at 25 °C in a wet air atmosphere with a relative humidity (80 RH%) on the same TMA system being connected with a precise humidity generator (Shinyei Technology, SRG-1R-1). In order to avoid moisture condensation in the sample chamber, the relative humidity was increased very slowly from 50 to 80% and maintained at 80% for 15–20 h until the specimen length was stabilized.

Storage modulus (E') and loss energy (E'') were measured as a function of temperature to determine T_g from the peak temperatures in the E'' curve on the same TMA system at a heating rate of 5 °C/min with a sinusoidal load frequency of 0.1 Hz in a nitrogen atmosphere. Thermal stability of PEsI films was estimated from the 5% weight loss temperatures (T_d^5) by thermogravimetric analysis (Bruker-AXS, TG-DTA2000) at a heating rate of 10 °C/min in nitrogen and air atmosphere.

The extent of water absorption (W_A %) for PEsI films was determined from the relation:

$$W_A = (W - W_0) / W_0 \times 100 \quad (1)$$

where W_0 is the weight of the samples vacuum-dried at 50 °C for 24 h, and W is the weight of the samples immersed in water at 23 °C for 24 h and subsequently wiped well with a tissue paper.

The imide contents (wt%) were calculated from the relation:

$$F_W (\text{imide}) / F_W (\text{unit}) \times 100 \quad (2)$$

where F_w (imide) and F_w (unit) denote the formula weights of the imide group (O=C–N–C=O) and the repeating units, respectively.

Tensile modulus (E), tensile strength (σ_b), and the elongation at break (ϵ_b) of the PI specimens (3 mm wide and 30 mm long, sample numbers > 15) were measured on a stretching testing machine (A & D, Tensilon UTM-II) at a crosshead speed of 8 mm/min.

3. Results and Discussion

3.1 Film properties of TAHQHB-based PEI systems

TAHQHB (HO–X–OH = HQ in **Figure 2**) showed excellent reactivity with various common aromatic diamines, 1,4-phenylenediamine (*p*-PDA) and 4,4'-ODA as suggested from very high $[\eta]_{\text{PAA}}$ values ranging 1.8–2.2 dL/g for the PEAs.

Table 1 summarizes the film properties of TAHQHB-based PEI films together with the TAHQ/*p*-PDA system studied in our early stage for a comparison. The TAHQHB/*p*-PDA film, as well as the TAHQ/*p*-PDA system, achieved an excellent combined properties, namely, an extremely low CTE (–2.0 ppm/K), considerably high T_g at 378 °C, good thermo-oxidative stability ($T_d^5 = 481$ °C in air), and the highest level of non-flammability (UL-94, V-0 class), although these *p*-PDA-based PEI

Tetracarboxylic dianhydride	Diamine	$[\eta]_{\text{PAA}}$ (dL/g)	T_g (°C)	CTE (ppm/K)	E (GPa)	ϵ_b (%)	W_A (%)	CHE (ppm/K)	T_d^5 (air) (°C)	UL94 V-0
TAHQHB	<i>p</i> -PDA	2.2	378	–2.0	6.32	7.2	0.54	2.9	481	passed
	4,4'-ODA	1.8	338	55.4	2.77	30.0	0.60	3.2	460	–
	<i>p</i> -PDA (40) + 4,4'-ODA (60)	1.9	335	24.1	4.63	11.1	0.49	1.8	467	–
TAHQ	<i>p</i> -PDA	3.7	ND	0.8	8.86	8.8	1.25	7.4	499	passed

films were both not always tough as suggested from an ϵ_b value lower than 10%, which is related to relatively poor chain entanglement arising from their very high backbone stiffness/linearity. The most striking features of the TAHQHB/*p*-PDA system are significantly decreased water absorption ($W_A = 0.54\%$) and CHE (2.9 ppm/RH%) compared with the TAHQ/*p*-PDA system. One of the primary factors for the reduced W_A and CHE is the decreased content of the highly polarized imide groups in the structure (18.2 wt% for the present system and 26.4 wt% for the TAHQ/*p*-PDA system).

Table 1. Properties of TAHQHB-based PEI films.

In order to control the CTE value, copolymerization approach was carried out with a common flexible diamine, 4,4'-ODA. The *p*-PDA(60); 4,4'-ODA(40) copolymer showed a still low CTE value of 24 ppm/K in addition to other excellent properties, particularly, a further decreased CHE (1.8 ppm/RH%) as listed in **Table 1**. But in this case, the copolymerization approach was not so effective for toughening in spite of its relatively high 4,4'-ODA content (40 mol%). This means that, as far as TAHQHB is used, to further improve the film toughness by copolymerization is not promising from the viewpoints of CCL applications since the use of 4,4'-ODA with higher contents is supposed to cause a significant CTE increase as an origin of CCL curling.

3.2 Effect of methyl substituent on film properties.

TAMPHB (HO–X–OH = M-HQ in **Figure 2**) showed also good reactivity with *p*-PDA and 4,4'-ODA

($[\eta]_{\text{PAA}} = 1.4\text{--}3.8$ dL/g for the PE_sAA_s). **Table 2** summarizes the film properties of the methyl-substituted TAMPHB-based PEI films. The TAMPHB/*p*-PDA film also displayed a considerably low CTE (5.0 ppm/K) and a very high T_g at 400 °C as well as the non-substituted counterpart. One notices that the incorporation of the methyl substituent was effective for reducing W_A as suggested from the fact that $W_A = 0.39\%$ for TAMPHB/*p*-PDA and 0.54% for non-substituted TAHQHB/*p*-PDA. A similar trend is also observed in a comparison between the 4,4'-ODA-based counterparts. This effect is probably attributed to denser chain packing or higher crystallinity as suggested from our previous work; the methyl-substituted TAHQ/M-APAB film, which possesses a lower W_A than the non-substituted TAHQ/APAB, showed a much more intensive and a sharper WAXD reflection peak than TAHQ/APAB. The substituent effect can be interpreted as the result that the presence of the methyl substituent allowed higher molecular motion for chain rearrangement during the thermal imidization process. Thus, the results revealed that the water absorption of PEIs is influenced by not only the structural factor (the imide content in the structures) but also the morphological factor (degree of molecular packing or crystallinity). In the present cases, the structural factor is probably preferential rather than the morphological one, since there seems to be practically no significant difference of the morphologies in our PEI systems consisting of rigid backbone structures as studied for CCL applications. This hypothesis does not conflict with a relatively good correlation between W_A and the imide group content in the structures as plotted in **Figure 3**.

Table 2. Properties of TAMPHB-based PEI

Tetracarboxylic dianhydride	Diamine	$[\eta]_{\text{PAA}}$ (dL/g)	T_g (°C)	CTE (ppm/K)	ε_b (%)	W_A (%)	CHE (ppm/K)	T_d^5 (air) (°C)	UL94 V-0
TAMPHB	<i>p</i> -PDA	3.8	400	5.0	14.8	0.39	2.9	442	–
	4,4'-ODA	1.4	325	72.6	51.5	0.30	–	438	–
	<i>p</i> -PDA (80) + 4,4'-ODA (20)	1.8	343	11.4	30.7	0.36	4.3	440	NG

Another feature of the methyl-substituted TAMPHB-based PEI systems is seen in relatively good toughness. Even the TAMPHB/*p*-PDA film exhibited $\varepsilon_b = 15\%$ in spite of its stiff/linear backbone structure. On the basis of a very high ε_b value of 52% for homo TAMPHB/4,4'-ODA system, copolymerization with 4,4'-ODA is expected to improve drastically the film toughness of the TAMPHB/*p*-PDA film while keeping the low CTE comparable to that of copper foil. As expected, the *p*-PDA(80);4,4'-ODA(20) copolymer displayed excellent combined properties as shown in **Table 2**. However, this approach failed in achieving the highest level of non-flammability when 16 μm thick specimens were used, probably owing to the presence of the methyl substituent.

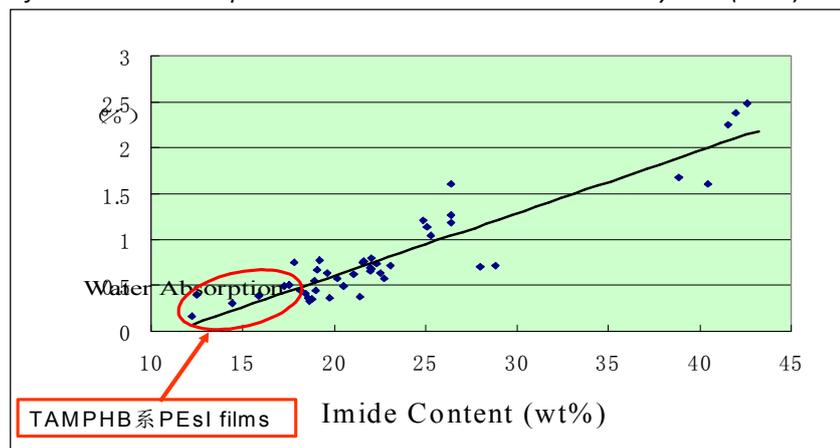


Figure 3. Relationship between the imide content and the water absorption for various

3.3 Effect of incorporation of *p*-biphenylene unit on film properties

Our next approach is to introduce *p*-biphenylene unit into the PEI backbones, by which non-flammability is expected to be improved. TA44BPHB (HO-X-OH = 4,4'-BP in **Figure 2**) showed also good reactivity with *p*-PDA and 4,4'-ODA ($[\eta]_{\text{PAA}} = 2.4\text{--}3.7$ dL/g for the PEAs). **Table 3** summarizes the film properties of TA44BPHB-based PEI films. The TA44BPHB/*p*-PDA film possessed similar properties to the TAHQHB/*p*-PDA film, i.e., an extremely low CTE (-5.0 ppm/K), a high T_g at 359 °C in addition to $\epsilon_b < 10\%$. The negative CTE characteristics can be sometimes observed for amorphous and highly in-plane-oriented PI films [6]. Probably, the present TA44BPHB/*p*-PDA system is also in a similar situation. Fortunately, in contrast to the TAHQHB-based systems, copolymerization with 4,4'-ODA was quite effective to improve the film toughness of the TA44BPHB/*p*-PDA system. The *p*-PDA(60);4,4'-ODA(40) copolymer showed excellent combined properties with good non-flammability comparable to the TAHQHB-based PEIs.

Table 3. Properties of TA44BPHB-based PEI films.

Tetracarboxylic Dianhydride	Diamine	$[\eta]_{\text{PAA}}$ (dL/g)	T_g (°C)	CTE (ppm/K)	E (GPa)	ϵ_b (%)	W_A (%)	CHE (ppm/K)	T_d^5 (air) (°C)	UL94 V-0
TA44BPHB	<i>p</i> -PDA	2.4	359	-5.0	7.03	6.5	0.43	6.7	459	passed
	4,4'-ODA	2.2	331	37.6	2.46	42.9	0.35	2.1	479	—
	<i>p</i> -PDA (60) + 4,4'-ODA (40)	2.6	363	10.2	4.17	24.0	0.51	3.3	476	passed

Figure 4 shows the structure–non-flammability (V-0) relationship as plotted for our PEI systems examined in this work. A trend was observed although the sample numbers are not so many; the incorporation of the ester groups exceeding ca. 14 wt% failed in achieving the highest level of non-flammability (UL-94, V-0). The result also unexpectedly suggests that the presence of methyl substituents was not always crucial factor for the non-flammability.

More recently, we prepared a novel phosphorus-containing tetracarboxylic dianhydride as shown in **Figure 5**. The use of these monomers for copolymerization enhanced furthermore the non-flammability of PEIs even at a very low content (only 5 mol% or less) without sacrificing other target properties as suggested from a drastically shortened burning time.

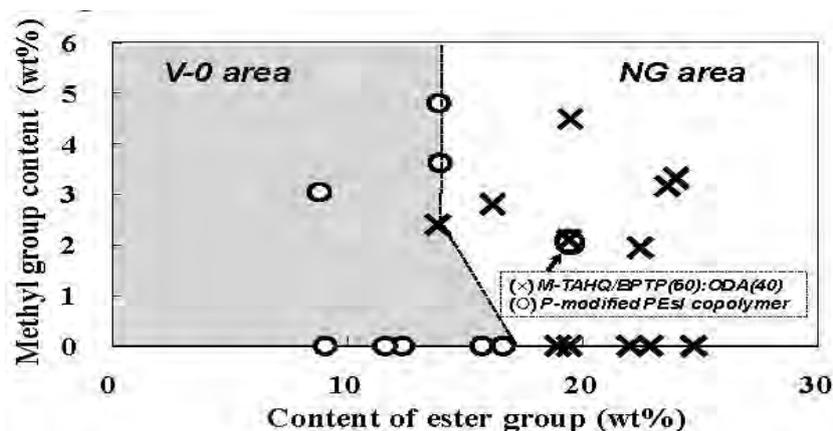


Figure 4. Influence of chemical composition of PEsIs on non-flammability: (○) V-0

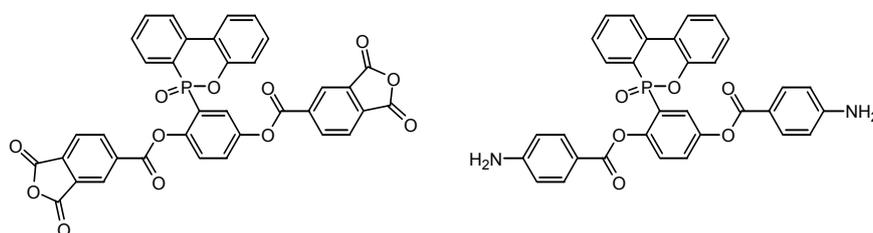


Figure 5. Phosphorus-containing monomers synthesized in this

3.4 Strategy for decreasing modulus of PEsi films

A recent trend for FPC is to suppress the spring-back property of FPCs. A simple approach to solve this problem is thinning of each layers of FPC (copper foils, base films, and cover layer). It is also effective to decrease the modulus of the base films themselves for this purpose. However, it is in principle difficult to simultaneously achieve low CTE and low modulus characteristics because the molecular design addressed to low CTE, i.e., the combination of stiff/linear backbone structures and a high degree of chain alignment usually causes the enhancement of the tensile modulus [9]. In this work, we propose novel naphthalene-containing PEsi systems with a lower aspect ratio. Another feature of the tetracarboxylic dianhydride monomer used here is in its asymmetric structure. We investigated various PEsi systems using this monomer. The chain structure is depicted in **Figure 6** as an example. **Table 4** summarizes the properties of the naphthalene-containing PEsi copolymer system. The results suggest that the present approach is effective to achieve a low CTE close to that of copper foil and a relatively low tensile modulus (E) while keeping other excellent combined properties.

Table 4. Properties of naphthalene-containing PEsi copolymer

$[\eta]_{\text{PAA}}$ (dL/g)	T_g (°C)	CTE (ppm/K)	E (GPa)	ϵ_b (%)	W_A (%)	CHE (ppm/K)	T_d^5 (air) (°C)
3.39	331	16.8	3.99	20.4	0.27	3.0	439

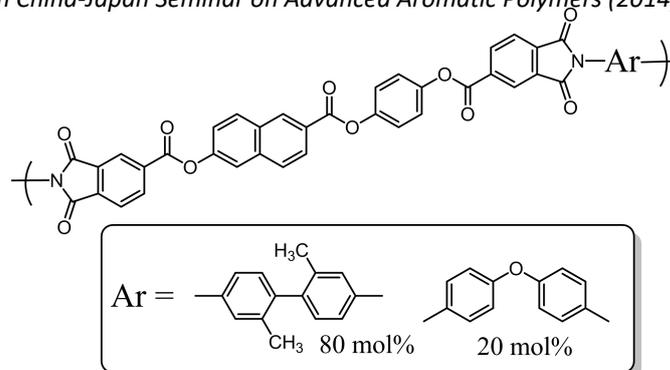


Figure 6. Naphthalene-containing PEI copolymer

4. Conclusions

Some novel ester-containing tetracarboxylic dianhydrides, where more than five numbers of aromatic rings are connected via para-ester linkages, provided higher-performance CCL base film materials possessing low CTEs comparable to that of copper foil, considerably low CHFs, sufficient film toughness, and non-flammability at the same time. The structure–non-flammability (V-0) relationship for our PEIs led to a temporal conclusion that PEIs with the ester group contents exceeding ca. 14 wt% in the structures cannot achieve the highest level of non-flammability (UL-94, V-0). In order to solve this problem, we developed novel phosphorus-containing monomers. Copolymerization using them at a minor content drastically improved the non-flammability without sacrificing other target properties. The present work also proposed a molecular design to simultaneously achieve low CTE and low modulus, i.e., the combination of incorporation of a bulky naphthalene unit with a lower aspect ratio and an asymmetric structure.

5. References

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