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Graphical Abstract

Symmetric and asymmetric spiro-type colorless poly(ester imide)s with low coefficients of thermal expansion, high glass transition temperatures, and excellent solution-processability

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Solution casting of the material shown in the figure led to a colorless film with a low yellowness index (3.4), a considerably low coefficient of thermal expansion (10.5 ppm K⁻¹), a very high T_g (351 °C), and a high tensile modulus (6.12 GPa).



Image display devices

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Symmetric and asymmetric spiro-type colorless poly(ester imide)s with low coefficients of thermal expansion, high glass transition temperatures, and excellent solution-processability

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Abstract

In this work, we present several new poly(ester imide)s (PEsIs) with low coefficients of thermal expansion (CTE), excellent optical transparency, very high heat resistance (T_g) , film ductility, and solution-processability. Symmetric and asymmetric spiro-type tetracarboxylic dianhydrides containing ester linkages (TA-s-Spiro and TA-a-Spiro) and diamines (AB-s-Spiro and AB-a-Spiro) were synthesized using xanthene-based isomeric bisphenols with a fluorenyl side group. The chemically imidized PEsIs were highly soluble in various common solvents including less polar non-amide solvents, and yielded stable solutions with high solid contents. The properties of the spiro-type PEsIs were systematically investigated and compared with those of the cardo-type counterparts. A PEsI derived from 1,2,3,4-cyclobutanetetraccarboxylic dianhydride (CBDA), AB-a-Spiro, and 2,2'-bis(trifluoromethyl)benzidine (TFMB) achieved outstanding combined properties, i.e., a very low CTE (10.5 ppm K⁻¹), excellent optical transparency (YI = 3.4, T_{400} = 80.8%), a very high T_g (351 °C) and solution-processability. Thus, the PEsIs are promising candidates as novel plastic substrates for use in image display devices. The isomer effects on the properties were also investigated and a possible mechanism for these effects is proposed.

Keywords: Poly(ester imide)s; Spiro structure; Cardo structure; Optical transparency; Coefficient of thermal expansion (CTE); Solution processability; Heat-resistant plastic substrates

1. Introduction

Heat-resistant colorless polymers are key materials for use in optical and optoelectronic applications. Colorless plastic substrate materials have been investigated as alternatives to current inorganic glass substrates to allow the upsizing of display devices and concomitant weight saving, as well as the realization of foldable or curved displays. These plastic substrates must have very high short-term heat resistance (i.e., glass transition temperature: $T_g > 300$ °C, desirably > 350 or 400 °C) to support the high-temperature processes used in device fabrication. Therefore, even poly(ether sulfone) (PES), which has the highest T_g (225 °C [1]) among commercially available super-engineering plastics, is not always suitable as the plastic substrates. On the other hand, wholly aromatic polyimides (PIs) are reliable heat-resistant polymers, and some have very high $T_{\rm g}$ values, exceeding 350 °C [2–7]. However, wholly aromatic PI films are in general intensely colored because of charge-transfer (CT) interactions [8], which often limit their optical and optoelectronic applications. Therefore, optically transparent (colorless) PIs and other high-temperature polymers have been studied in academia and industry as promising candidate plastic substrates [9-32]. The most effective strategy for eliminating PI film coloration is to disturb the CT interactions by using aliphatic (usually cycloaliphatic) monomers either diamines or tetracarboxylic dianhydrides or both [8–27].

The plastic substrates for optoelectronics must also have excellent dimensional stability

during the multiple thermal cycles used in the device fabrication processes; this can be achieved by significantly reducing their linear coefficients of thermal expansion (CTE) in the film plane (X-Y) direction in the glassy temperature regions ($< T_g$). However, non-stretched polymer films prepared by solution casting or melt extrusion molding usually show high CTE values (50–120 ppm K⁻¹ [**33**] because of the practically three-dimensionally random chain orientation, which causes significant thermal expansion–contraction behavior during thermal cycling. This causes serious problems, such as misalignment and adhesion failure of various micro-components, laminate warpage, and transparent electrode breakdown.

A low thermal expansion property is achieved when there is a high degree of chain alignment in the X-Y direction (in-plane orientation), which prominently occurs during the thermal imidization of PI precursor [poly(amic acid)s (PAAs)] films formed on substrates only when the PI systems have linear and rigid backbone structures [34-37]. However, previously reported cycloaliphatic monomers with structural linearity/planarity, which is favorable for inducing prominent in-plane orientation, are practically limited to trans-1,4-cyclohexanediamine (t-CHDA) and 1,2,3,4-cyclobutanetetracarboxylic dianhydride (CBDA). For example, the combination of t-CHDA and rigid aromatic tetracarboxylic dianhydrides [e.g., 3,3'4,4'-biphenyltetracarboxylic dianhydride (s-BPDA)] provides colorless PI films with very low CTE values [38,39], as shown in Fig. 1. However, the use of t-CHDA causes the formation of

poorly soluble salts in anhydrous solvents (usually amide solvents such as N,N-dimethylacetamide (DMAc)] in the initial stages of the PAA polymerization process, which often results in the termination of PAA polymerization or greatly extends the reaction periods until the reaction mixture becomes homogeneous [21,27,39,40]. In contrast, there is no salt formation problem when CBDA was combined with rigid aromatic diamines [typically, 2,2'-bis(trifluoromethyl)benzidine (TFMB)], and this system leads to a colorless PI film with a relatively low CTE through the conventional two-step process (PAA casting on a substrate + thermal imidization) [38]. However, the imidized forms of these transparent low-CTE systems are not soluble in common solvents.

We have previously revealed that a somewhat complicated film preparation method via chemical imidization (i.e., chemical imidization at room temperature in solution + isolation of the PI powder + re-dissolution in fresh solvents + coating/drying) is superior to the conventional process (PAA solution coating/drying + thermal imidization at elevated temperatures) in terms of achieving both optical transparency and a low CTE in the resultant PI films [**27**]. This means that compatibility with the chemical imidization process holds the key to achieving our present goals. The chemical imidization process can also be applied to highly soluble PI systems. Otherwise, on the addition of a dehydrating agent [acetic anhydride (Ac₂O)/pyridine mixture] to PAA solutions during chemical imidization, the reaction mixtures become inhomogeneous with gelation or

precipitation of the half-imidized portion, and subsequent casting from a homogeneous PI solution is inhibited. Unfortunately, the above-mentioned semi-aromatic transparent PIs are not compatible with the chemical imidization process because of their insolubility.

A variety of solubility-improving groups, linkages, and structural units have been reported in the literature, e.g., bulky and non-polarized substituents (CF₃ [10,23,28,41–45], *tert*-butyl [46], and phenyl side groups [47,48]), highly polar and bent connecting groups (–SO₂– groups [32,49]), highly twisted/distorted units (2,2'-biphenyl group [50]), bent and asymmetric structural units [51,52], non-planar cycloaliphatic units [19], and cardo structures [53,54]. However, these approaches for solubility improvement mostly reduce in the chain linearity/rigidity, consequently sacrificing the low CTE.

We have previously reported that poly(ester imide)s (PEsIs) obtained using ester-linked cardo-type tetracarboxylic dianhydride with 9-fluorenyl (FL) side group (TA-BPFL, **Fig. 1**) show enhanced solubility compared to the corresponding cardo-type poly(ether imide)s [**55**]. For example, the combination of TA-BPFL and *t*-CHDA (**Fig. 1**) led to a PEsI soluble in hot *N*-methyl-2-pyrrolidone (NMP) [**55**], even though *t*-CHDA-based PIs are usually quite insoluble. The significantly improved solubility of TA-BPFL/*t*-CHDA is probably attributed to a combined effect of the ester linkages and the bulky FL side group of TA-BPFL, which has a perpendicularly directed molecular plane to the main chains, as shown in **Fig. 1**. However, the TA-BPFL/*t*-CHDA

PEsI film did not show low CTE behavior, probably reflecting the "hinge" structure at the central sp^3 carbon atom of TA-BPFL (**Fig. 1**), which significantly reduces the overall chain linearity, consequently, the in-plane chain orientation was disturbed. The results motivated us to modify TA-BPFL to create a local coplanar structure by the formation of ether-bridge between the two 9-phenolic groups on the FL unit [i.e., formation of a xanthene (XAN) unit with a spiro structure], whereby the local molecular planarity/linearity can be enhanced.

One study [56] reported that poly(ether imide)s derived from an ether-linked spiro-type diamine containing a XAN unit and common aromatic tetracarboxylic dianhydrides showed good solubility and relatively high T_g values, although the CTE was not reported. As discussed later, this type of poly(ether imide) does not usually have low CTE values owing to their decreased overall main chain linearity. On the other hand, our target monomers, i.e., ester-linked spiro-type monomers with a FL-pendant XAN unit have the potential to improve the low CTE property while maintaining excellent solubility (i.e., compatibility with chemical imidization process). In this study, we investigated the effects of symmetric spiro-type monomers with ester linkages on the current target properties (transparency, solubility, CTE, and T_g) and compared them with those of the asymmetric counterparts. The results suggest that some of the spiro-type PEsIs developed in this work are promising novel plastic substrate materials for use in image display devices and other optoelectronic materials.

2. Experimental

2.1. Materials

2.1.1. Monomer synthesis

Spiro(fluorene-9,9'-xanthene]-3',6'-diol (s-Spiro FLBP)

Spiro-type bisphenols and related monomers were synthesized using raw materials listed in Supplementary Data 1. First, we carried out the synthesis of a symmetric spiro-type bisphenol (s-Spiro FLBP, Fig. 2) without solvent [56] or in toluene [57]. The previously reported synthetic procedures gave rise to an orange- or yellow-colored product, which was the mixtures of the desired bisphenol and a minor fraction of a dimeric by-product estimated by liquid chromatography-mass spectrometry (Fig. 2). The latter is probably responsible for the intense coloration of the product. Then we carried out the synthesis by a sophisticated method using water as a solvent [58]; 9-fluorenone (9-FLN, 39.12 mmol), resorcinol (RC, 313.79 mmol), and 1-dodecanethiol (1.56 mmol) was suspended in water (5.75 mL) in a 300 mL-flask and heated at 55-60 °C. To the reaction mixture, conc. HCl (8.47 mL) was added very slowly, and refluxed at 55-60 °C for 8 h with continuous stirring. Subsequently, water (43.1 mL) was added and neutralized with a NaOH aqueous solution in an ice bath. The pale pink precipitate formed was collected by filtration, washed with water, and dried at 120 °C for 12 h under vacuum. The

product was dissolved in 2-propanol, and an undissolved portion was filtered out. Subsequently, the product was recrystallized from a mixed solvent (2-propanol/water, 4/1, v/v), and dried at 100 °C for 12 h under vacuum (total yield: 74 %). The analytical data of the product is as follows. FT-IR (KBr plate method, cm⁻¹): 3505/3405 (O–H), 3061/3036 (C_{arom}-H), 1262/1171 (C_{arom}-O-Carom). ¹H-NMR [400 MHz, dimethyl sulfoxide (DMSO)-d₆, δ, ppm]: 9.61 [s, 2H (the measured relative integrated intensity: 2.00H), OH], 7.92 [d, 2H(2.04H), J = 7.6 Hz, 4,5-protons of the fluorene (FL) unit], 7.37 [t, 2H (2.07H), J = 7.4 Hz, 3,6-protons of FL], 7.22 [t, 2H (2.07H), J = 7.5 Hz, 2,7-protons of FL], 7.02 [d, 2H (2.03H), J = 7.6 Hz, 1,8-protons of FL], 6.58 [sd, 2H (2.04H), J = 2.4 Hz, 4,5-protons of the xanthene (XAN) unit], 6.26 [dd, 2H (2.01H), J = 8.6, 2.4Hz, 2,7-protons of XAN], 6.03 [d, 2H (2.00H), J = 8.6 Hz, 1,8-protons of XAN]. Elemental analysis: Calcd. (%) for C₂₅H₁₆O₃ (364.40 g mol⁻¹): C, 82.40; H, 4.43, Found: C, 82.47; H, 4.52. Melting point determined from an endothermic peak by differentia scanning calorimetry (DSC): 265 °C. These data confirmed that the product is the desired 3,6-dihydroxy-substituted form (s-Spiro FLBP) shown below.



Spiro(fluorene-9,9'-xanthene)-2',6'-diol (a-Spiro FLBP)

An asymmetric-type isomer of s-Spiro FLBP, a-Spiro FLBP, was synthesized using 9-FLN (32 mmol), RC (157 mmol), and hydroquinone (HQ, 157 mmol) in the same way as the procedures for the synthesis of s-Spiro FLBP. Thin-layer chromatography (TLC) using silica gel and CHCl₃/ethyl acetate (6/1, v/v) as an eluent for the product showed four spots with the $R_{\rm f}$ values of 0.67 (obscure), 0.58, 0.39, and 0 (obscure), which correspond to 2,7-, 2,6-, and 3,6-dihydroxy-substituted compounds, and predicted dimeric compound, respectively (Fig. 2). Column chromatography (Wakogel C-300, $\phi = 40-64 \mu m$) using a mixed eluent (CHCl₃/ethyl acetate, 12/1, v/v) was effective for isolating the desired 2,6-dihydroxy-substituted form (a-Spiro FLBP); a single spot ($R_f = 0.58$) was observed on TLC after this procedure. An oily product was obtained after solvent evaporation of the separated fraction. The oily product turned into a powder form by addition of *n*-hexane and successive solvent removal. The solid product was washed with water and dried at 100 °C for 12 h under vacuum. The analytical data of the pale-yellow product obtained is as follows. FT-IR (KBr plate method, cm⁻¹): 3512/3446 (O-H), 3059/3034/3010 (Carom-H), 1240 (Carom-O-Carom). ¹H-NMR [400 MHz, DMSO-*d*₆, δ, ppm]: 9.59 [s, 1H (1.00H), 6-OH], 8.91 [s, 1H (1.07H), 2-OH], 7.95 [d, 2H (2.07H), J = 7.6 Hz, 4,5-protons of FL], 7.39 [t, 2H (2.07H), J = 7.5 Hz, 3,6-protons of FL], 7.24 [t, 2H (2.05H), J = 7.5 Hz, 2,7-protons of FL], 7.09-7.05 [m, 3H (3.09H), 1,8-protons of FL + 4-proton of XAN], 6.61 [dd,

1H (1.06H), J = 8.8, 2.9 Hz, 3-protons of XAN], 6.57 [sd, 1H (1.08H), J = 2.4 Hz, 5-protons of XAN], 6.25 [dd, 1H (1.07H), J = 8.4, 2.3 Hz, 7-protons of XAN], 6.03 [d, 1H (1.03H), J = 8.6 Hz, 8-protons of XAN], 5.65 [sd, 1H (1.08), J = 2.9 Hz, 1-proton of XAN]. Elemental analysis: Calcd. (%) for C₂₅H₁₆O₃ (364.40 g mol⁻¹): C, 82.40; H, 4.43, Found: C, 82.00; H, 4.50. Melting point (DSC): 228 °C. These data confirmed that the product is the desired 2,6-dihydroxy-substituted form (*a*-Spiro FLBP) shown below.



Ester-linked s-spiro-type tetracarboxylic dianhydride (TA-s-Spiro)

An ester-linked *s*-spiro-type tetracarboxylic dianhydride was synthesized according to the reaction scheme shown in **Fig. 3**. *s*-Spiro FLBP (10.01 mmol) was dissolved in anhydrous tetrahydrofuran (THF, 47.1 mL) in the presence of pyridine (60 mmol, 4.85 mL) as an HCl acceptor in a sealed flask with a septum cap. In a separate sealed flask, trimellitic anhydride chloride (TMAC, 30.09 mmol) was dissolved in THF (16.6 mL). To the TMAC solution cooled at 0 °C, the *s*-Spiro FLBP solution was slowly added using a syringe with continuous magnetic stirring, after which the reaction mixture was stirred at room temperature for 12 h. The precipitate

formed was collected by filtration and washed with THF and subsequently water. The white product was dried at 160 °C for 12 h to ensure cyclodehydration of a hydrolyzed portion (yield: 67%). The analytical data of the product is as follows. FT-IR (KBr plate method, cm^{-1}): 3066 (Carom-H), 1856/1782 (anhydride C=O), 1739 (ester C=O), 1493 (phenyl), 1224/1168 (Carom-O-C_{arom}), and the absence of the absorption bands at 3400–3500 cm⁻¹ (O–H) from the unreacted s-Spiro FLBP and ~2600 cm⁻¹ (hydrogen-bonded carboxylic acid O-H) from the hydrolyzed product. ¹H-NMR [400 MHz, DMSO-*d*₆, δ, ppm]: 8.62–8.58 [m, 4H (4.01H), 3,3'- + 5,5'-protons of the phthalic anhydride (PAn) unit], 8.27 [d, 2H (2.02H), J = 7.8 Hz, 6,6'-protons of PAn], 8.04 [d, 2H (2.00H), J = 7.8 Hz, 4,5-protons of FL], 7.49–7.46 [m, 4H (4.01H), 3,6-protons of FL + 4,5-protons of XAN], 7.32 [t, 2H (2.02H), J = 7.6 Hz, 2,7-protons of FL], 7.21 [d, 2H (2.02H), J = 7.6 Hz, 1,8-protons of FL], 6.94 [d, 2H (2.00H), J = 8.6 Hz, 2,7-protons of XAN], 6.40 [d, 2H (2.03H), J = 8.6 Hz, 1,8-protons of XAN]. Elemental analysis: Calcd. (%) for C₄₃H₂₀O₁₁ (712.63 g mol⁻¹): C, 72.47; H, 2.83, Found: C, 72.61; H, 2.96. Melting point (DSC): 331 °C. These data confirmed that the product is the desired compound (TA-s-Spiro) shown below.



The abbreviations, purification methods, and melting points for all the spiro-type monomers synthesized in this work are summarized in **Supplementary Data 2**.

For a comparison, ester-linked cardo-type counterpart (TA-Cardo, **Fig. 3**) was also synthesized in a similar manner. The analytical data are shown in **Supplementary Data 3**.

Ester-linked a-spiro-type tetracarboxylic dianhydride (TA-a-Spiro)

An isomer of TA-*s*-Spiro, TA-*a*-Spiro (**Fig. 3**), was synthesized from *a*-Spiro FLBP (5.03 mmol) and TMAC (15.01 mmol) in anhydrous acetone in the presence of pyridine. After the reaction, the solvent was removed, and the pale-yellow solid obtained was washed with toluene and subsequently water, and dried at 200 °C for 12 h under vacuum. The crude product was recrystallized from a mixed solvent (toluene/acetic anhydride, 25/2, v/v), and vacuum-dried at 200 °C for 12 h (total yield: 50%). The analytical data is follows. FT-IR (KBr plate method, cm⁻¹): 3066 (C_{arom}-H), 1863/1780 (anhydride C=O), 1760/1736 (ester C=O), 1488 (phenyl), 1223 (ester C-O), 1163 (C_{arom}-O-C_{arom}), and the absence of the absorption bands at 3400–3500 cm⁻¹ (O-H) from the unreacted *a*-Spiro FLBP and ~2600 cm⁻¹ (hydrogen-bonded carboxylic acid O-H) from the hydrolyzed product. ¹H-NMR [400 MHz, DMSO-*d*₆, δ ppm]: 8.62–8.59 [m, 2H (2.09H), 3,6-protons of PAn], 8.48–4.44 [m, 2H (2.02H), 3',6'-protons of PAn], 8.27 [d, 1H(1.07H), *J* = 7.8 Hz, 5-proton of PAn], 8.15 [d, 1H (1.00H), *J* = 7.8 Hz, 5'-proton of PAn],

8.01 [d, 2H (2.00H), J = 7.6 Hz, 4,5-protons of FL], 7.49–7.44 [m, 4H (4.03H), 3,6-protons of FL + 3,5-protons of XAN], 7.36–7.30 [m, 3H (3.05H), 2,7-protons of FL + 4-proton of XAN], 7.22 [d, 2H (2.04H), J = 7.6 Hz, 1,8-protons of FL], 6.92 [dd, 1H (1.00H), J = 8.6, 2.3 Hz, 7-proton of XAN], 6.36–6.34 [m, 2H (2.01H), 1,8-protons of XAN]. Elemental analysis: Calcd. (%) for C₄₃H₂₀O₁₁ (712.63 g mol⁻¹): C, 72.47; H, 2.83, Found: C, 72.44; H, 3.16. Melting point (DSC): 294 °C. These data confirmed that the product is the desired compound (TA-*a*-Spiro) shown below.



Ester-linked s-spiro-type diamine (AB-s-Spiro)

AB-*s*-Spiro was synthesized according to the reaction scheme shown in **Fig. 3**. The detailed procedures are as follows. 4-Nitrobenzoyl chloride (4-NBC, 30.0 mmol) was dissolved in anhydrous THF (9.4 mL) in a sealed flask. In another sealed flask, *s*-Spiro FLBP (10.02 mmol) was dissolved in anhydrous THF (47.1 mL) in the presence of pyridine (60 mmol). To the 4-NBC solution cooled to 0 $^{\circ}$ C, the *s*-Spiro FLBP solution was slowly added using a syringe with continuous magnetic stirring, after which the reaction mixture was stirred at room temperature for

12 h. The pale-yellow precipitate formed was collected by filtration and washed with a small quantity of THF, a large quantity of water, and methanol, and vacuum-dried at 120 °C for 12 h (yield: 68%). The analytical data of the product as follows. FT-IR (KBr plate method, cm^{-1}): 3075 (Carom-H), 1742 (ester C=O), 1522/1347 (NO₂), 1486 (phenyl), 1239/1152 (Carom-O-Carom), and the absence of the absorption bands at 3400-3500 (O-H) from unreacted s-Spiro FLBP. ¹H-NMR [400 MHz, DMSO- d_6 , δ , ppm]: 8.41 [d, 4H (4.04H), J = 9.0 Hz, 2,2',6,6'-protons of the nitrobenzene (NB) unit], 8.34 [d, 4H (4.03H), J = 9.0 Hz, 3,3',5,5'-protons of NB], 8.04 [d, 2H (2.01H), J = 7.6 Hz, 4,5-protons of FL], 7.47 [t, 2H (2.04H), J = 7.5 Hz, 3,6-protons of FL], 7.42 [sd, 2H (2.03H), *J* = 2.4 Hz, 4,5-protons of XAN], 7.31 [t, 2H (2.04H), *J* = 7.5 Hz, 2,7-protons of FL], 7.20 [d, 2H (2.00H), J = 7.5 Hz, 1,8-protons of FL], 6.89 [dd, 2H (2.05H), J = 8.6, 2.4 Hz, 2,7-protons of XAN], 6.39 [d, 2H (2.00H), J = 8.6 Hz, 1,8-protons of XAN]. Melting point (DSC): 292 °C. These data confirmed that the product is the desired dinitro compound (NB-s-Spiro) shown below.



The nitro groups of NB-s-Spiro were reduced as follows. NB-Spiro (5.80 mmol) was

dissolved in N,N-dimethylformamide (DMF, 100 mL) and Pd/C (0.424 g) as a catalyst was added to this solution. The reaction mixture was refluxed at 100 °C for 4 h in a hydrogen atmosphere and cooled to room temperature. After the catalyst residue was filtered out, the filtrate was concentrated by an evaporator, and water (200 mL) was added to the flask. The white precipitate formed was collected by filtration, washed with water and methanol, and dried at 120 °C for 12 h under vacuum (yield: 81%). The analytical data of the product as follows. FT-IR (KBr plate method, cm⁻¹): 3480/3375/3218 (amine N-H), 3066 (Carom-H), 1708 (ester C=O), 1628 (NH₂, deformation), 1517/1489 (phenyl), 1237/1172 (Carom-O-Carom). ¹H-NMR [400 MHz, DMSO-d₆, δ , ppm]: 8.01 [d, 2H (2.01H), J = 7.5 Hz, 4,5-protons of FL], 7.77 [d, 4H (4.05H), J = 8.7 Hz, 3,3',5,5'-protons of the aniline (AN) unit], 7.46 [t, 2H (2.03H), J = 7.4 Hz, 3,6-protons of FL], 7.31 [t, 2H (2.04H), J = 7.5 Hz, 2,7-protons of FL], 7.20 [sd, 2H (2.02H), J = 2.3 Hz, 4,5-protons of XAN], 7.17 [d, 2H (2.02H), J = 7.6 Hz, 1,8-protons of FL], 6.74 [dd, 2H (2.02H), J = 8.5, 2.3 Hz, 2,7-protons of XAN], 6.62 [d, 4H (4.04H), J = 8.7 Hz, 2,2',6,6'-protons of AN], 6.32 [d, 2H (2.03H), J = 8.6 Hz, 1,8-protons of XAN], 6.19 [s, 4H (4.00H), NH₂]. Elemental analysis: Calcd. (%) for C₃₉H₂₆O₅N₂ (602.65 g mol⁻¹): C, 77.73; H, 4.35; N, 4.65, Found: C, 77.52; H, 4.50; N, 4.67. Melting point (DSC): 274 °C. These data confirmed that the product is the desired diamine (AB-s-Spiro) shown below.



For a comparison, ester-linked cardo-type counterpart (AB-Cardo, **Fig. 3**) was also synthesized in a similar manner. The analytical data are shown in **Supplementary Data 4**.

Ester-linked a-spiro-type diamine (AB-a-Spiro)

An isomer of AB-*s*-Spiro, AB-*a*-Spiro (**Fig. 3**), was synthesized using *a*-Spiro FLBP in a similar manner to that in the synthesis of the symmetric counterpart. A pale-yellow product was obtained from *a*-Spiro FLBP and 4-NBC with a yield of 70%. The analytical data of the product is as follows. FT-IR (KBr plate method, cm⁻¹): 3076 (C_{arom}–H), 1737 (ester C=O), 1524/1348 (NO₂), 1490 (phenyl), 1177 (C_{arom}–O–C_{arom}), and the absence of the absorption bands at 3400–3500 (O–H) from unreacted *a*-Spiro FLBP. ¹H-NMR [400 MHz, DMSO-*d*₆, δ , ppm]: 8.42 [d, 2H (2.05H), *J* = 8.9 Hz, 2,6-protons of NB], 8.34 [d, 2H (2.02H), *J* = 8.9 Hz, 3,5-protons of NB], 8.29 [d, 2H (2.01H), *J* = 8.8 Hz, 2',6'-protons of NB], 8.19 [d, 2H (2.02H), *J* = 9.0 Hz, 3',5'-protons of NB], 8.01 [d, 2H (2.05H), *J* = 7.6 Hz, 4,5-protons of FL], 7.48–7.43 [m, 3H (3.02H), 3,6-protons of FL + 3-proton of XAN], 7.41 [sd, 1H (1.02H), *J* = 2.4 Hz, 5-proton of

XAN], 7.33–7.29 [m, 3H (3.05H), 2,7-protons of FL + 4-proton of XAN], 7.21 [d, 2H (2.03H), J = 7.6 Hz, 1,8-protons of FL], 6.88 [dd, 1H (1.04H), J = 8.6, 2.4 Hz, 7-proton of XAN], 6.35 [d, 1H (1.01H), J = 8.6 Hz, 8-proton of XAN], 6.27 [sd, 1H (1.00H), J = 2.8 Hz, 1-proton of XAN]. Melting point (DSC): 301 °C. These data confirmed that the product is the desired dinitro compound (NB-*a*-Spiro) shown below.



The catalytic reduction of NB-*a*-Spiro was carried out in the same way as the procedures used for the symmetric counterpart and a white product was obtained with a yield of 86%. The analytical data of the product is as follows. FT-IR (KBr plate method, cm⁻¹): 3459/3363/3217 (amine N–H), 3060 (C_{arom}–H), 1714 (ester C=O), 1631 (NH₂, deformation), 1516/1479 (phenyl), 1167 (C_{arom}–O–C_{arom}). ¹H-NMR [400 MHz, DMSO-*d*₆, δ , ppm]: 7.99 [d, 2H (2.06H), *J* = 7.5 Hz, 4,5-protons of FL], 7.77 [d, 2H (2.05H), *J* = 8.7 Hz, 3,5-protons of AN], 7.52 [d, 2H (2.02H), *J* = 8.8 Hz, 3',5'-protons of AN], 7.44 [t, 2H (2.05H), *J* = 7.5 Hz, 3,6-protons of FL], 7.39 [d, 1H (1.02H), *J* = 8.9 Hz, 4-proton of XAN], 7.30 [t, 2H (2.01H), *J* = 7.6 Hz, 2,7-protons of FL], 7.22 [sd, 1H (1.01H), *J* = 2.4 Hz, 5-protons of XAN], 7.19 [d, 2H (2.03H), *J* = 7.5 Hz, 1,8-protons of FL], 7.15 [dd, 1H (1.07H), J = 8.9, 2.7 Hz, 3-proton of XAN], 6.73 [dd, 1H (1.02H), J = 8.6, 2.4 Hz, 7-protons of XAN], 6.63 [d, 2H (2.01H), J = 8.8 Hz, 2,6-protons of AN], 6.52 [d, 2H (2.08H), J = 8.8 Hz, 2',6'-protons of AN], 6.29 [d, 1H (1.02H), J = 8.5 Hz, 8-proton of XAN], 6.20 [s, 2H (2.00H), 1-NH₂], 6.13 [s, 2H (2.05H), 1'-NH₂], 6.03 [sd, 1H (1.00H), J = 2.7 Hz, 1-proton of XAN]. Elemental analysis: Calcd. (%) for C₃₉H₂₆O₅N₂ (602.65 g mol⁻¹): C, 77.73; H, 4.35; N, 4.65, Found: C, 77.25; H, 4.48; N, 4.78. Melting point (DSC): 292 °C. These data confirmed that the product is the desired diamine (AB-*a*-Spiro) shown below.



Ether-linked s-spiro-type diamine (AP-s-Spiro)

For comparison with ester-linked *s*-spiro-type diamine, an ether-linked counterpart was synthesized according to the reaction scheme shown in **Supplementary Data 5**. The detailed procedures are as follows. *s*-Spiro-FLBP (12.66 mmol) and 4-fluoronitrobenzene (4-FNB) were dissolved in DMAc (30 mL) in the presence of K_2CO_3 (29.60 mmol), and refluxed at 160 °C for 4 h in a nitrogen atmosphere. The reaction mixture was slowly poured into a large quantity of water. The pale-yellow precipitate formed was collected by filtration, washed with water, and

dried at 120 °C for 12 h under vacuum (yield: 98%). The analytical data of the product is as follows. FT-IR (KBr plate method, cm⁻¹): 3070 (C_{arom}–H), 1522/1343 (NO₂), 1483 (phenyl), 1230/1150 (C_{arom}–O–C_{arom}), and the absence of the absorption bands at 3400–3500 (O–H) from unreacted *s*-Spiro FLBP. ¹H-NMR [400 MHz, DMSO-*d*₆, δ , ppm]: 8.26 [d, 4H (4.06H), *J* = 9.3 Hz, 2,2',6,6'-protons of NB], 8.02 [d, 2H (2.00H), *J* = 7.6 Hz, 4,5-protons of FL], 7.46 [t, 2H (1.99H), *J* = 7.5 Hz, 3,6-protons of FL], 7.32 [t, 2H (1.90H), *J* = 7.6 Hz, 2,7-protons of FL], 7.21–7.17 [m, 6H (6.05H), 3,3',5,5'-protons of NB + 1,8-protons of FL], 7.13 [sd, 2H (2.05H), *J* = 2.5 Hz, 4,5-protons of XAN], 6.72 [dd, 2H (2.05H), *J* = 8.6, 2.5 Hz, 2,7-protons of XAN], 6.37 [d, 2H (2.04H), *J* = 8.6 Hz, 1,8-protons of XAN]. Melting point (DSC): 190 °C. These data confirmed that the product is the desired dinitro compound (NP-*s*-Spiro) shown below.



NP-Spiro (12.4 mmol) was dissolved in 1,4-dioxane (75 mL) in the presence of Pd/C (0.746 g), and refluxed at 80 °C for 8 h in a hydrogen atmosphere. After the catalyst residue was filtered out, the filtrate was slowly poured into a large quantity of water. The white precipitate formed was collected by filtration, washed with water and methanol, and recrystallized from toluene

(yield: 42%). The analytical data of the product as follows. FT-IR (KBr plate method, cm⁻¹): 3431/3353/3216 (amine N–H), 3044/3011 (C_{arom}–H), 1609 (NH₂, deformation), 1509/1489 (phenyl), 1210/1168 (C_{arom}–O–C_{arom}). ¹H-NMR [400 MHz, DMSO-*d*₆, δ ppm]: 7.95 [d, 2H (2.00H), *J* = 7.5 Hz, 4,5-protons of FL], 7.40 [t, 2H (2.04H), *J* = 7.4 Hz, 3,6-protons of FL], 7.24 [t, 2H (1.99H), *J* = 7.5 Hz, 2,7-protons of FL], 7.07 [d, 2H (1.91H), *J* = 7.5 Hz, 1,8-protons of FL], 6.77 [d, 4H (3.94H), *J* = 6.7 Hz, 3,3',5,5'-protons of AN], 6.61–6.56 [m, 6H (5.87H), 4,5-protons of XAN + 2,2',6,6'-protons of AN], 6.38 [dd, 2H (1.96H), *J* = 8.6, 2.5 Hz, 2,7-protons of XAN], 6.15 [d, 2H (1.99H), *J* = 8.7 Hz, 1,8-protons of XAN], 5.02 [s, 4H (3.75H), NH₂]. Elemental analysis: Calcd. (%) for C₃₇H₂₆O₃N₂ (546.63 g mol⁻¹): C, 81.30; H, 4.79; N, 5.12, Found: C, 81.67; H, 4.92; N, 5.15. Melting point (DSC): 233 °C. These data confirmed that the product is the desired diamine (AP-*s*-Spiro) shown below.



For a comparison, ether-linked cardo-type counterpart (AP-Cardo, **Supplementary Data 5**) was also synthesized in a similar manner. The analytical data are shown in **Supplementary Data 6**.

Commercially available common monomers (Fig. 4) were also used in this study. These

abbreviations, commercial sources, purification methods, and melting points are summarized in **Supplementary Data 1**.

2.1.2. Polyaddition, imidization, and film preparation

The polymerization of PAAs, imidization, and PI film preparation were carried out according to the schemes shown in **Fig. 5**. A typical procedure for the polyaddition is as follows. Tetracarboxylic dianhydride powder (5 mmol) was added to an N,N-dimethylacetamide (DMAc) of diamine (5 mmol) with continuous stirring in a sealed bottle. The reaction mixture (initial solute content: 30 wt%) was stirred at room temperature, if necessary, while conducting multiple dilution with a minimal quantity of DMAc at each step, and a homogeneous/viscous PAA solution was obtained after 72 h.

Chemical imidization was carried out by slowly adding a dehydrating agent $(Ac_2O/pyridine, 7/3, v/v)$ to an adequately diluted PAA solution at a fixed feed ratio of $[Ac_2O]/[COOH]_{PAA} = 5$ with continuous vigorous stirring, followed by stirring at room temperature for 24 h in a sealed bottle. The homogenous reaction mixture obtained was adequately with DMAc and very slowly poured into a large amount of poor solvent (methanol or water) to form fibrous precipitates, and collected by filtration, washed with methanol, and dried at 100 °C for 12 h under vacuum. The chemically imidized powder samples were dissolved in a fresh anhydrous solvent [e.g.,

cyclopentanone (CPN), DMAc, or *N*-methyl-2-pyrrolidone (NMP)] at a solid content of 8–20 wt%, if necessary, while warming to facilitate dissolution. The homogeneous PEsI solutions obtained were coated on a glass substrate, and dried at 60 °C for 2 h (for CPN and DMAc) or 80 °C for 3 h [for γ -butyrolactone (GBL) and NMP] in an air convection oven, followed by vacuum-drying at 200 °C for 1 h on the substrate. After being peeling off from the substrate, the PEsI films (typically 20 µm thick) were heated at an annealing temperature [T_{ann} , typically at 250 °C (or 300 °C)] for 1 h under vacuum to remove residual stress. These thermal conditions during the film preparation were adjusted to obtain better-quality films.

For some insoluble systems, PEsI films were prepared upon thermal imidization as follows. PAA solution was coated on a substrate, dried 60 °C for 2 h, heated typically at 200 °C for 1 h + 300 °C for 1 h under vacuum on the substrate, followed by annealing at 300 °C (or 330 °C) for 1 h under vacuum without the substrate. These thermal conditions were also adjusted to obtain better-quality films.

In this paper, the chemical compositions of PEsI systems are represented with the abbreviations of the monomer components used [tetracarboxylic dianhydrides (A) and diamines (B)] as A/B for homopolymers and $A_1; A_2/B_1; B_2$ for copolymers.

2.2. Measurements

2.2.1. Inherent viscosity and molecular weight

The reduced viscosities (η_{red}) of PAAs and chemically imidized PEsIs were measured in DMAc at a solid content of 0.5 wt% at 30 °C on an Ostwald viscometer. The polyelectrolyte effect of PAAs disturbs to determine the inherent viscosities (η_{inh}) from the extrapolation to zero concentration. Therefore, the η_{red} values of PAAs are often treated as the η_{inh} values. For highly soluble PEsI systems in THF, the number- (M_n) and weight- (M_w) average molecular weights were determined by gel permeation chromatography (GPC) using THF as an eluent at room temperature on a Jasco, LC-2000 Plus HPLC system with a GPC column (Shodex, KF-806L) at a flow rate of 1 mL min⁻¹ by ultraviolet-visible detection at 300 nm (Jasco, UV-2075). The calibration was performed using standard polystyrenes (Shodex, SM-105).

2.2.2. Linear coefficient of thermal expansion

The CTE values along the film plane (*X*–*Y*) direction for PEsI specimens (15 mm long, 5 mm wide, and typically 20 μ m thick) in the glassy region were measured by the thermomechanical analysis (TMA) as an average in the range of 100–200 °C at a heating rate of 5 °C min⁻¹ on a thermomechanical analyzer (Netzsch, TMA 4000) with a fixed static load (0.5 g per unit film thickness in μ m, i.e., 10 g load for 20 μ m-thick films) in a dry nitrogen atmosphere. In this case, after the preliminary first heating run up to 120 °C and successive cooling to room temperature in

the TMA chamber, the data were collected from the second heating run to remove an influence of adsorbed water. The TMA curve was also used for determining the T_g of PEsI films, as mentioned later.

2.2.3. Heat resistance

The storage modulus (E') and loss energy (E'') of PEsI films were measured by the dynamic mechanical analysis (DMA) at a heating rate of 5 °C min⁻¹ at a sinusoidal load frequency of 0.1 Hz with an amplitude of 15 gf in a nitrogen atmosphere on the TMA instrument (as before). The T_g of PEsI films was determined from the peak temperature of the E'' curve (method-1). The T_g was also determined from an inflection point of the TMA curve measured under a fixed static load, where the specimens started to abruptly elongate, as an intersection of two tangential lines (method-2).

The thermal stability of PEsI films was evaluated from the 5% weight loss temperatures (T_d^5) by the thermogravimetric analysis (TGA) on a thermo-balance (Netzsch, TG-DTA2000). TGA was performed at a heating rate of 10 °C min⁻¹ in dry nitrogen and air atmosphere. A small weight loss due to the desorbed water from the samples was observed around 100 °C in the TGA curves. It was compensated by off-set at 150 °C to 0% weight loss for the data analysis.

2.2.4. Optical properties

The light transmission spectra of PEsI films (typically 20 µm thick) were recorded on an ultraviolet-visible spectrophotometer (Jasco, V-530) in the wavelength (λ) range of 200–800 nm. The light transmittance at 400 nm (T_{400}) and the cut-off wavelength (λ_{cut}) at which the transmittance becomes practically null were determined from the spectra. In this work, the transmittance data at longer wavelengths (e.g., 450 and 500 nm) themselves were not discussed because they are often less informative for evaluating the film coloration; the films are not always colorless even if the T_{500} value was very high ($T_{500} > 80\%$). The yellowness indices (YI, ASTM E 313) for PEsI films were also determined from the spectra under a standard illuminant of D65 and a standard observer function of 2° using a color calculation software (Jasco) on the basis of the relationship:

$$YI = 100 (1.2985x - 1.1335z) / y$$
 (1)

where *x*, *y*, and *z* are the CIE tristimulus values. YI takes zero for an ideal white/transparent sample. The total light transmittance (T_{tot} , JIS K 7361-1) and the diffuse transmittance (T_{diff} , JIS K 7136) of PEsI films were measured on a double-beam haze meter equipped with an integrating sphere (Nippon Denshoku Industries, NDH 4000). The haze (turbidity) of PEsI films was calculated from the relationship:

$$Haze = (T_{diff} / T_{tot}) \times 100$$
(2)

The in-plane (n_{in} or n_{xy}) and out-of-plane (n_{out} or n_z) refractive indices of PEsI films were measured with a sodium lamp at 589.3 nm (*D*-line) on an Abbe refractometer (Atago, 4T, n_D range: 1.47–1.87) equipped with a polarizer by using a contact liquid (sulfur-saturated methylene iodide $n_D = 1.78-1.80$) and a test piece ($n_D = 1.92$). The birefringence of PEsI films, which indicates the relative extent of chain alignment in the *X*–*Y* direction, was calculated from the relationship:

$$\Delta n_{\rm th} = n_{\rm in} - n_{\rm out}$$

(3)

2.2.5. Mechanical properties

The tensile modulus (*E*), tensile strength (σ_b), and elongation at break (ε_b) of PEsI films were measured using specimens free of any defects such as fine bubbles (30 mm long, 3 mm wide, typically 20 µm thick) on a mechanical testing machine (A & D, Tensilon UTM-II) at a cross head speed of 8 mm min⁻¹ at room temperature. The data analysis was carried out on a data processing program (Softbrain, UtpsAcS Ver. 4.09) and averaged for the valid run numbers (n >15) unless stated otherwise.

2.2.6. Solubility

The solubility of PEsIs was qualitatively examined using chemically imidized powder

samples by observing whether the samples (10 mg) were completely dissolved in various solvents (1 mL) in a test tube at room temperature (1st step). The insoluble samples were heated at an established temperature for each solvent (2nd step). For the samples that were dissolved by heating, the solution homogeneity was monitored after cooling to room temperature.

3. Results and discussion

3.1. PEsIs from symmetric spiro-type tetracarboxylic dianhydride (TA-s-Spiro)

To ascertain the potential of TA-*s*-Spiro, which has a unique feature, a "locally planar and bulky" structure, we first investigated homo-PEsIs derived from TA-*s*-Spiro and common diamines. The results are summarized in **Table 1**. TA-*s*-Spiro had sufficient PAA polymerizability with 4,4'-oxydianiline (4,4'-ODA), *p*-phenylenediamine (*p*-PDA), 4,4'-diaminobenzanilide (DABA), and TFMB, as suggested by the relatively high η_{inh} values ranging from 0.96–1.53 dL g⁻¹. These PAAs were chemically imidized and maintained a homogeneous state during the reaction, except for the system using *p*-PDA. The results reflect the good solubility of the imidized forms, which arises because the bulky FL side groups act to inhibit chain flocculation. A typical ¹H-NMR spectrum for the chemically imidized samples is shown in **Fig. 6**. Chemical imidization occurred quantitatively, as suggested from the absence of signals corresponding to the NHCO protons at $\delta = 10$ –11 ppm and COOH protons at $\delta = 13$ –14 ppm, which should be observed if a non-imidized portion remains. Complete imidization was also confirmed from the FT-IR spectra (Jasco, FT/IR 4100 infrared spectrometer). A typical FT-IR spectrum for the chemically imidized samples is shown in **Supplementary Data 7**, which includes the following characteristic bands (cm⁻¹): 3066 (C_{arom}–H), 1784 (imide C=O), 1732 (imide C=O + ester C=O), 1489 (1,4-phenylene), 1370 (imide N–C_{arom}), 1310/1175 (C–F), and 723 (imide ring deformation). No traces of PAA-specific bands (broad O–H stretching band for the hydrogen-bonded dimeric COOH groups around 2600 cm⁻¹ and amide C=O stretching bands at 1680/1530 cm⁻¹) were detected. The chemically imidized TA-*s*-Spiro-based PEsIs maintained relatively high η_{inh} values, corresponding to relatively high molecular weights [e.g., $M_w = 1.12 \times 10^5$, $M_n = 5.09 \times 10^4$, $M_w/M_n = 2.20$, and $\eta_{inh} = 1.17$ dL g⁻¹ for TA-*s*-Spiro/TFMB (system **#5-1**)].

The chemically imidized powder samples for PEsIs derived from TA-*s*-Spiro and aromatic diamines, except for *p*-PDA, were soluble in various common organic solvents at room temperature, as summarized in **Table 2**, where the solvents used in the qualitative solubility tests are arranged from left in order of empirical dissolution power for PIs. They were also soluble in less polar (less hygroscopic) solvents, such as triglyme (TriGL), at room temperature, despite their poor dissolution ability for PIs. These systems provided stable PEsI solutions with high solid contents (**Table 1**), which are necessary for the subsequent solution casting process. The excellent solubility is attributed to the bulky FL unit with a perpendicularly directed molecular

plane to the XAN plane (**Fig. 2**), which disturbs close chain stacking. The casting solvents (GBL and CPN) did not significantly influence the properties of the PEsI films, as shown in the comparison between systems **#5-1** and **#5-2** (**Table 3**).

The TA-s-Spiro-based PEsI films exhibited high T_g values, as listed in **Table 1**; for example, the T_g was 292 °C even when a flexible ether-linked 4,4'-ODA (system #1) was used as a diamine. This high- T_g characteristic, which is similarly observed in the cardo-type counterparts [55], results from the restricted internal rotation of the main chains because of the presence of the large/planar FL side group, which has a large sweep volume for internal rotation. However, significant film coloration was inevitable for this PEsI film (#1), as indicated by its low T_{400} value and very high YI value (Table 1). This is attributed to the CT interactions between the trimellitimide (TMI) units (electron acceptor) and N-aromatic units (electron donor) originating from the diamines in the PEsI main chains, as schematically drawn at the bottom of Table 1. The PEsI film (#1) did not have a low CTE (54.1 ppm K^{-1}) like those commonly observed in 4,4'-ODA-based PI systems [59]. This is ascribed to the decreased overall chain linearity induced by the introduction of flexible ether linkages and consequently disturbed in-plane orientation during the solution casting process. On the other hand, the use of the diamines with rigid/linear structures (e.g., p-PDA, DABA, and TFMB) is expected to be effective in reducing the CTE. However, the use of p-PDA (system #2) was unsuccessful for this purpose, which is probably

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related to the fact that this PEsI film was prepared by the conventional two-step process (thermal imidization of the PAA cast film) because of the insolubility for chemical imidization. The PEsI film from p-PDA (#2) was also highly colored.

A possible approach to obtain a low CTE while avoiding intense coloration is to use *t*-CHDA, which behaves like *p*-PDA in terms of structural stiffness/linearity [**38,39**]. The polyaddition of TA-*s*-Spiro and *t*-CHDA (system **#3**) resulted in salt formation in the initial reaction stages, but a homogeneous and viscous PAA solution was finally obtained by heating the salt-containing reaction mixture at 100 °C for a short period, followed by stirring without additional heating. Unfortunately, after the solution casting of the PAA, thermal imidization yielded a significantly cracked film, which disturbed subsequent property evaluations. This is probably due to poor chain entanglement arising from the insufficient initial molecular weight of the PAA.

In contrast to the *p*-PDA system (#2), the TA-*s*-Spiro/DABA system (#4) could be chemically imidized. As expected, the resultant PEsI cast film exhibited an appreciably decreased CTE (39.5 ppm K⁻¹) compared to that of the 4,4'-ODA system (54.1 ppm K⁻¹), although this PEsI film (#4) was also highly colored. On the other hand, the use of TFMB (system #5-1) significantly improved the optical transparency, as suggested from its dramatically reduced YI value (3.7), with an appreciable decrease in the CTE, although there is room for further improvement in the low CTE. This PEsI film (#5-1) was also ductile with resistance to the 180° bending test at a practically null curvature radius and had low water uptake (0.40%). Thus, the combination of TA-*s*-Spiro and TFMB has the potential to achieve our goal.

The properties of the TA-s-Spiro/TFMB system (#5-1) were compared with those of the cardo-type counterpart (#6) (Table 1). Recall that s-spiro-type monomers have a "locally planar and bulky" structural feature, whereas the structures of the corresponding cardo-type monomers are regarded as "non-planar/bent and bulky". As expected, the TA-s-Spiro/TFMB film (#5-1) exhibited a much higher T_g (323 °C) than that of the TA-Cardo/TFMB film (#6, $T_g = 285$ °C) and additionally, an appreciably lower CTE (45.6 ppm K^{-1}) than that of the latter (50.7 ppm K^{-1}). To confirm these trends, the comprehensive comparisons were made for all the related systems examined in this study. Fig. 7(a) shows the relationship of the T_g values for the spiro systems (Y-axis) and those for cardo systems (X-axis). All the plots are positioned in the region above the Y = X line. This indicates that the FL-pendant spiro structure is superior to the corresponding cardo structure in terms of the T_g of the PEsI films. The observed trend very likely results from the ether-bridging in the XAN unit, which completely prevents the internal rotation of two phenolic units connected to the $9-sp^3$ carbon atom on the FL side group.

A similar comparison was carried out for the CTE, as shown in **Fig. 7(b)**. All the plots are positioned in the region below the Y = X line. The results mean that the spiro structure is advantageous in decreasing the CTE compared to the corresponding cardo structure. This can

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also be interpreted as the effect of ether-bridging, whereby two phenolic units are coplanarized to create a XAN structure; consequently, the overall main chain linearity is somewhat increased.

Fig. 7(c) shows a similar comparison for the optical transparency. The plots are positioned almost on the Y = X line or slightly below. This suggests that the ether-bridging does not significantly reduce the optical transparency.

The solubility of the chemically imidized spiro-type PEsIs was also compared with that of the cardo-type counterparts. In a limited comparison between TA-*s*-Spiro/TFMB (**#5-1**) and TA-Cardo/TFMB (**#6**), these were both quite soluble in various solvents without heating and no practical difference was observed in the qualitative solubility tests (**Table 2**).

3.2. Modification of TA-s-Spiro/TFMB by copolymerization

To improve the target properties further, we carried out structural modifications of the TA-*s*-Spiro/TFMB system (**#5-1**) by copolymerization with selected tetracarboxylic dianhydrides (6FDA, PMDA, NTDA, and CBDA). The properties of the TA-*s*-Spiro/TFMB-based copolymers are summarized in **Table 3**. The chemically imidized powder samples of all the PEsI copolymers listed here were highly soluble in common solvents, even when typical rigid tetracarboxylic dianhydrides such as PMDA and NTDA were used as the modifiers, as shown in **Table 2**, and provided stable PEsI solutions with high solid contents. Copolymerization with 6FDA (50 mol%,

#7) was effective in improving the optical transparency, as indicated by the significantly increased T_{400} and decreased YI (Table 3). This effect is reasonable from the fact that the 6FDA/TFMB homo-PI film is almost colorless [10,28]. However, this approach also had a negative effect: an appreciable increase in the CTE. This is attributed to the sterically bent hinge structure of the 6FDA-based diimide units [60,61], which reduces the overall main chain linearity that is indispensable for achieving an in-plane chain orientation. On the other hand, the modification using PMDA (#8) is expected to be effective in reducing the CTE. However, no positive effect was observed for the CTE, as shown in Table 3. This is possibly an effect of the molecular weight on the CTE; i.e., a decrease in the molecular weights tends to cause a decrease in the degree of in-plane orientation during the solution casting process [21]. The use of PMDA as the comonomer also gave rise to a significant increase in coloration, which is inevitable because of a very strong electron-accepting character of the PMDA-based diimide units in the main chains [8]. Thus, the modifications using these common tetracarboxylic dianhydrides (6FDA and PMDA) were both unsuccessful in terms of improving the optical transparency and low CTE property simultaneously.

In contrast, NTDA, another modifier, displayed quite different behavior; copolymerization with NTDA (30 mol%, **#9**) resulted in a significant decrease in the CTE (33.5 ppm K^{-1}) without reducing the optical transparency and solubility (chemical imidization process compatibility), as
shown in **Table 3**. A further increase in the NTDA content in the copolymer to 40 mol% (**#10**) achieved a low CTE (26.1 ppm K⁻¹) with a slightly improved T_{400} (52.4%) and a high T_g (320 °C). A similar unexpected positive effect of using the NTDA modifier was also observed in other systems, and a possible mechanism has been proposed by us previously [**28–30**].

In the approach using CBDA as another modifier, our initial concern was that the resultant copolymers might lose compatibility with the chemical imidization process because of the significant decrease in the solubility, which is based on the fact that CBDA-based PIs are mostly insoluble [23]. Contrary to the above-mentioned concern, the PEsI copolymer (#11) derived from TA-s-Spiro (50 mol%), CBDA (50 mol%), and TFMB maintained good solubility (Table 2), as well as compatibility with the chemical imidization process. The DMAc-cast film of the CBDA-modified copolymer (#11) achieved significantly improved optical transparency (T_{400} = 66.7% and YI = 3.3), an enhanced T_g (345 °C), and a dramatically reduced CTE (29.0 ppm K⁻¹) compared to those of the pristine homo-PEsI (#5-1), although its thermal stability (T_d^5) was decreased somewhat because of the partial use of cycloaliphatic CBDA. The increase in the CBDA content to 70 mol% in the copolymer enabled us to reduce the CTE (27.9 ppm K^{-1}) further without significantly affecting the other target properties. It is interesting to note that the CBDA-modified copolymer (#11) possessed a lower YI value than that of the CBDA/TFMB homo-PI system (#28, YI = 4.0). This can be attributed to the difference in the film preparation

route; the latter required heating at an elevated temperature (330 °C) to complete thermal imidization, which is unfavorable in terms of suppressing coloration. In contrast, the copolymer film (#11) could be formed by drying and annealing at a much lower temperature ($T_{ann} = 250$ °C). Thus, the results emphasize the importance of chemical imidization process compatibility.

A comparison between the CBDA-modified spiro-type copolymer system (#11) and the cardo-type counterpart (#12) revealed that the former is superior to the latter in terms of reducing the CTE and enhancing the T_{g} .

3.3. PEsIs from symmetric spiro-type diamine (AB-s-Spiro) and related copolymers

In the next approach, an ester-linked *s*-spiro-type diamine (AB-*s*-Spiro) was used. CBDA, which was synthesized by the photodimerization of maleic anhydride, has a crank-shaft-like steric structure with a relatively high structural linearity/rigidity [14], as shown in Fig. 4. The cycloaliphatic CBDA-based diimide (CBDI) units in the PI main chains also have a similar rigid structure, which is suitable for improving the low CTE property and optical transparency of the resultant PI films. Therefore, in this study, CBDA was chosen as a tetracarboxylic dianhydride for combination with AB-*s*-Spiro, although there is a concern that the use of CBDA as the tetracarboxylic dianhydride component alone may reduce the compatibility with the chemical imidization process. Table 4 summarizes the properties of AB-*s*-Spiro-based PEsIs and related

systems. Contrary to our concern, CBDA/AB-s-Spiro homo-PEsI (#12) was compatible with the chemical imidization process, and the PEsI powder obtained was soluble in various solvents at room temperature, as shown in Table 5. The CPN-cast PEsI film had dramatically enhanced optical transparency ($T_{400} = 79.2\%$), which is due to the inhibited CT interactions obtained by using non-aromatic tetracarboxylic dianhydride (CBDA). This PEsI film also displayed an extremely high T_g of 371 °C and a relatively low CTE (39.0 ppm K⁻¹), as listed in Table 4. Among the **PEsIs** obtained using the symmetric spiro-type monomers, the CBDA/AB-s-Spiro(50);TFMB(50) copolymer (#13) was an optimum system, possessing excellent combined properties, including excellent transparency ($T_{400} = 82.8\%$, YI = 3.7), a very high T_g (364 °C), and a significantly decreased CTE (26.0 ppm K⁻¹). The increase in the TFMB content to 60 mol% in the copolymer resulted in a further decrease in the CTE to 24.6 ppm K^{-1} .

In this work, the CBDA/AB-s-Spiro system (#12) was also compared with the related systems derived from CBDA with AB-s-Spiro analogues (AB-Cardo, AP-s-Spiro, and AP-Cardo). In contrast to the highly soluble CBDA/AB-s-Spiro system (#12), of which the structural feature is expressed as "ester + spiro", the CBDA/AB-Cardo system (#14, "ester + cardo") was incompatible with the chemical imidization process because the reaction mixture remained inhomogeneous by partial precipitation through the reaction, disturbing full imidization. On the other hand, the use of AP-s-Spiro (#16, "ether + spiro") allowed chemical imidization in a

homogeneous state. In contrast, the system using AP-Cardo (#17, "ether + cardo") failed to complete the chemical imidization owing to the above-mentioned inhomogenization problem. These results suggest that the spiro structure is superior to the cardo structure in terms of solubility, which was unexpected because the rigid/planar local structure of the XAN unit in the former would appear to be unfavorable for dissolution. These related systems were also modified by copolymerization with 50 mol% of TFMB (#13, #15, #18, #19), whereby the CBDA/AB-Cardo system (#14) became soluble and compatible with the chemical imidization process, although the CBDA/AP-Cardo(50);TFMB(50) copolymer system (#19) remained incompatible. The results suggest that the solubility-promoting ability of these FL-pendant analogous diamines decreases in the following order: AB-s-Spiro > AP-s-Spiro > AB-Cardo > AP-Cardo. The comparison between the soluble system (#15) and insoluble system (#19) also suggests that the ester connecting groups are more helpful in enhancing the resultant polymer solubility than the ether connecting groups. A similar connecting group effect on the polymer solubility was also observed for FL-pendant cardo-type PIs in our previous study [55].

3.4. PEsIs from asymmetric spiro-type tetracarboxylic dianhydride (TA-a-Spiro) and related copolymers

As described above, the introduction of the FL-pendant s-spiro structure into the PEsI

backbones was effective in enhancing the T_g and solubility and contributed somewhat to reducing the CTE. Our next approach, which was inspired by these results, was to reduce the CTE further by using isomers of the *s*-spiro-type monomers mentioned above. For this purpose, we synthesized an asymmetric structure of ester-linked spiro-type tetracarboxylic dianhydride (TA-*a*-Spiro, **Fig. 3**), which has a unique structural feature, i.e., "locally planar, linear, and bulky". To ascertain the potential of TA-*a*-Spiro, we first focused on homo-PEsIs derived from TA-*a*-Spiro and common diamines.

The properties of TA-*a*-Spiro-based PEsIs are summarized in **Table 6**. The dependence of the properties on the common diamines for the TA-*a*-Spiro-based systems was similar to that for the TA-*s*-Spiro-based counterparts. TA-*a*-Spiro showed relatively good PAA polymerizability with common diamines, except for *t*-CHDA, as suggested from the η_{inh} values, which exceed 1.0 dL g⁻¹. The TA-*a*-Spiro-based systems using aromatic diamines were basically compatible with chemical imidization process, except for when rigid *p*-PDA was used as the diamine, and the chemically imidized powder samples were soluble in various common solvents, as summarized in **Table 7**. The combination of TA-*a*-Spiro and aromatic diamines, as with the symmetric counterparts, inevitably led to colored PEsI films. The TA-*a*-Spiro-based PEsI films also maintained high T_g values. On the other hand, a peculiar feature to the TA-*a*-Spiro-based systems was observed; despite the use of the flexible, ether-containing 4,4'-ODA, the

TA-a-Spiro/4,4'-ODA system (#20) exhibited an appreciably decreased CTE (37.3 ppm K^{-1}) compared to that of the symmetric counterpart (#1, $CTE = 54.1 \text{ ppm } \text{K}^{-1}$). From the viewpoints of the resultant PEsI chain linearity, to use p-PDA instead of 4,4'-ODA should be advantageous for further decreasing the CTE. However, in fact, the TA-a-Spiro/p-PDA system (#21) showed an increased CTE (48.3 ppm K^{-1}) compared to the system using 4,4'-ODA (#20). This unexpected result is probably attributed to the fact that this PEsI film was prepared via thermal imidization after the casting of the PAA solution because of the absence of chemical imidization process compatibility. The observed negative effect on the CTE probably results from an increased contribution from orientational relaxation during thermal imidization at elevated temperatures. On the other hand, the combination of TA-a-Spiro and TFMB (#23) enabled us to apply chemical imidization; as a result, casting from the CPN solution and successive drying at much lower temperatures than those used for thermal imidization led to a PEsI film with a rather low CTE value (25.4 ppm K^{-1}). This result is attributed to the high degree of in-plane chain orientation induced during the solution casting processes, as suggested from the relatively high birefringence value ($\Delta n_{\rm th} = 0.059$). We have previously proposed that there is a close relationship between the backbone linearity of the graphically drawn extended chain forms, the extent of in-plane orientation, and the low CTE properties of the resultant PI films [21,62]. The present results are consistent with this concept; the TA-a-Spiro/TFMB system (#23) is undoubtedly composed of a backbone with high linearity, as shown in **Fig. 8(a)**, which was difficult to actualize without the present ester-linked tetracarboxylic dianhydride with an asymmetric structure. This PEsI film (#23) was ductile with resistance to the 180° bending test and had very low water uptake (0.08%).

In this system (**#23**), the optical transparency was also appreciably improved ($T_{400} = 28.9\%$, YI = 11.7) compared to that of the system using 4,4'-ODA (**#20**, $T_{400} = 3.1\%$, YI = 26.8), although the optical data obtained here were still much far from our target values ($T_{400} > 80\%$, YI < 4). In addition, copolymerization with 6FDA (**#24**) improved the optical transparency ($T_{400} = 46.6\%$, YI = 5.9). However, this approach also brought about an undesirable CTE increase (41.7 ppm K⁻¹).

3.5. PEsIs from asymmetric spiro-type diamine (AB-a-Spiro) and related copolymers

Our final approach was to combine a novel ester-linked FL-pendant diamine including the asymmetric spiro structure (AB-*a*-Spiro) with CBDA. This novel diamine has a unique structural feature, i.e., "locally planar, linear, and bulky". The properties of the resultant PEsI (#25) are summarized in **Table 8**. AB-*a*-Spiro diamine showed good PAA polymerizability with CBDA, as suggested by the relatively high η_{inh} value (0.94 dL g⁻¹). This system (#25) was suitable for the chemical imidization process, despite the use of CBDA alone as the tetracarboxylic dianhydrides,

which does not usually provide PIs with sufficient solubility for chemical imidization in many cases [27], as typically observed in the CBDA/TFMB system. Indeed, chemical imidization provided a PEsI soluble in amide solvents at room temperature (#25, Table 7). Thus, the results reveal that AB-*a*-Spiro, as well as the symmetric counterpart, maintains an effective solubility-promoting ability. The DMAc-cast film (#25) was perfectly colorless, as evidenced by a very high T_{400} value (83.8%), an extremely low YI value (1.7), and a very low haze (0.81%). However, this PEsI film was so brittle that it was difficult to prepare adequately sized high-quality films for mechanical testing and other measurements.

The CBDA/AB-*a*-Spiro system was modified by copolymerization with TFMB (50 mol%). This modification (**#26**) somewhat improved the solubility, as shown in **Table 7**. Casting from the DMAc solution afforded a free-standing ductile PEsI film, although the elongation at break obtained by tensile testing was not sufficiently high ($\varepsilon_{b max} = 6.0\%$) and was comparable to that of the CBDA/TFMB system (**#28**). The appearance of this PEsI film (**#26**) is shown at the bottom of **Table 8**. This film was almost colorless, as supported by its optical data ($T_{400} = 80.8\%$ and YI = 3.4). It is noteworthy that the PEsI cast film (**#26**) achieved a very low CTE (10.5 ppm K⁻¹). In addition, a further increase in the TFMB content in the copolymer to 60 mol% (**#27**) afforded a ductile PEsI film with resistance to the 180° bending test, and the film resulted in a further reduced CTE (9.8 ppm K⁻¹) while maintaining high transparency and a very high T_g . It is rare that

such low CTE values generated just by solution casting. The present results are undoubtedly attributed to the significant in-plane chain orientation induced during the solution casting process, as evidence by the high birefringence values ($\Delta n_{\rm th} = 0.073$ for **#26** and 0.077 for **#27**). The high extent of in-plane orientation was also responsible for the very high tensile modulus (E = 6.12 GPa) of the PEsI film (**#26**). These results correspond well to its very high backbone linearity in the extended chain forms, as depicted in **Fig. 8(b)**, which is an essential requirement for producing a low CTE. The PEsI film (**#26**) also exhibited a very high $T_{\rm g}$ (351 °C).

Thus, some of the PEsIs developed in this work, in particular, the PEsI (**#26**) are promising candidates as novel plastic substrate materials for use in image display devices and other high-temperature optoelectronic materials.

3.6. Comparison of the properties between symmetric and asymmetric spiro-type PEsIs

Fig. 9(a) shows the comparison of the T_g values between the symmetric (X-axis) and asymmetric spiro-type (Y-axis) systems. These plots are mostly positioned in the region below the Y = X line, indicating that the asymmetric spiro-type PEsIs tend to have lower T_g values than those of the symmetric counterparts, although the former still maintained very high T_g values. A difference in the T_g was specifically observed in the TA-Spiro-based systems rather than in the CBDA/AB-Spiro-based system [open symbol in **Fig. 9(a)**]. The results can be explained in terms of the difference in the "slewing range" of the internal rotation around the O–XAN linkages; the symmetric spiro system requires a larger slewing range for the rotation, which represents a higher obstacle for the rotational motion than for the rotation around the 2-substituted ether group on the XAN unit in the TA-*a*-Spiro-based counterparts, as schematically shown in **Supplementary Data 8**.

A similar comparison between the symmetric (X-axis) and asymmetric (Y-axis) systems was carried out for the CTE. As shown in **Fig. 9(b)**, all the plots are positioned in the region below the Y = X line, indicating the asymmetric spiro-type systems are undoubtedly superior to the symmetric counterparts in terms of reducing the CTE. The difference in the CTE was enlarged in the lower CTE region, as observed in the CBDA/AB-Spiro-based system [open symbol in **Fig. 9(b)**].

The optical transparency was also similarly compared using the T_{400} values. As shown in **Fig. 9(c)**, the plots for the TA-Spiro-based systems are positioned in the region below the Y = X line, indicating that the TA-*a*-Spiro-based PEsIs tend to show somewhat lower optical transparency than their symmetric counterparts. The results can be explained by assuming the presence of a weak intramolecular CT interaction between the central XAN unit (electron donor) and the TMI unit (electron acceptor), as discussed in our previous paper [**30**]. This assumption is compatible with the results of their dilute solutions (2.0×10^{-3} base M) in DMAc; the molar extinction coefficient at 400 nm was $\varepsilon_{400} = 16.5$ base M cm⁻¹ for TA-*a*-Spiro/TFMB and $\varepsilon_{400} = 4.9$ base M cm⁻¹ for TA-s-Spiro/TFMB (Supplementary Data 9). Therefore, the difference in the film transparency between the asymmetric and symmetric systems in Fig. 9(c) likely arises from the difference in the electron-donating ability of the *a*-FLBP and *s*-FLBP units; the former, consisting of hydroquinone (HQ) and resorcinol (RC) units, probably has a slightly higher electron-donating ability than the latter, which consists of two RC units, as schematically depicted in Supplementary Data 10. This consideration is based on the fact that the ionization potential of HQ is slightly lower than that of RC [63]. On the other hand, in the CBDA/AB-Spiro-based systems, it is reasonable to assume that, the 4-aminobenzoate unit adjacent to the FL-pendant XAN unit does not behave as a strong electron acceptor, unlike the TMI units. Indeed, there was almost no difference in the T_{400} values between the CBDA/AB-a-Spiro-based PEsI films and the s-Spiro-based counterparts [open symbols in Fig. 9(c)]. A similar result was also observed for their dilute solutions in DMAc (Supplementary Data 11).

However, these results indicate that the above-mentioned inferiority of *a*-spiro-type PEsIs in terms of the T_g and optical transparency almost disappeared in the CBDA/AB-*a*-Spiro-based systems while maintaining the overwhelming superiority of *a*-spiro-type PEsIs in lowering the CTE values.

4. Conclusions

Ester-linked *s*-spiro-type tetracarboxylic dianhydrides (TA-*s*-Spiro) and diamines (AB-*s*-Spiro) were synthesized using FL-pendant bisphenols with the XAN unit (*s*-FLBP). A series of PEsIs were prepared by polyaddition using these spiro-type monomers and subsequent chemical imidization in solutions. Most of TA-*s*-Spiro-based systems were compatible with the chemical imidization process, reflecting the sufficiently high solubility of their imidized forms. The PEsI powder samples obtained were highly soluble in various common solvents including less polar TriGL without heating and yielded stable solutions of CPN and GBL with high solid contents at room temperature.

The GBL-cast film of TA-*s*-Spiro/TFMB was less colored, as suggested by the low YI value (3.7), although there is room for improvement in its T_{400} value (48.3%). This PEsI film also displayed a rather high T_g (323 °C) and a slightly decreased CTE (45.6 ppm K⁻¹) compared to that of the TA-*s*-Spiro/4,4'-ODA film (CTE = 54.1 ppm K⁻¹). A comparison of the film properties between the spiro- and cardo-type PEsIs revealed that the former possessed much higher T_g values and appreciably lower CTE values than those of the latter. The results are attributed to an ether-bridging effect, which contributed to an increase in the overall main chain linearity/rigidity accompanied by the formation of a local coplanar XAN structure.

The TA-s-Spiro/TFMB system was modified by copolymerization with various

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tetracarboxylic dianhydrides. For example, copolymerization using CBDA (50 mol%) was effective in significantly reducing the CTE (29.0 ppm K⁻¹) and enhancing the optical transparency (YI = 3.3, T_{400} = 66.7%) while maintaining a very high T_g (345 °C) and good solubility.

An ester-linked spiro-type diamine (AB-*s*-Spiro) was also used to investigate the properties of the resultant PEsIs. The PEsI copolymer obtained from CBDA, AB-*s*-Spiro (50 mol%), and TFMB (50 mol%) achieved excellent combined properties, i.e., a low CTE (26.0 ppm K⁻¹), excellent optical transparency (YI = 3.7, T_{400} = 82.8%), an extremely high T_g (364 °C), film ductility (ε_b^{max} = 12.2%), and solution-processability.

Our approach to improving the target properties was extended to the isomeric spiro-type PEsI systems. For this purpose, asymmetric spiro-type monomers (TA-*a*-Spiro and AB-*a*-Spiro) were synthesized using an isomeric bisphenol (*a*-FLBP). A series of PEsIs were prepared using these *a*-spiro-type monomers via chemical imidization. For example, the CPN-cast film of TA-*a*-Spiro/TFMB exhibited a significantly low CTE (25.4 ppm K⁻¹), but this was accompanied by a decrease in the optical transparency and T_g , compared to those of the *s*-spiro-type counterpart. Possible mechanisms have been proposed to explain the reduction in the optical transparency and T_g by using TA-*a*-Spiro. On the other hand, the combination of AB-*a*-Spiro and CBDA almost canceled the above-mentioned inferiority while maintaining low CTE

characteristics. For example, the copolymer consisting of CBDA, AB-*a*-Spiro (50 mol%), and TFMB (50 mol%) achieved excellent combined properties, i.e., a very low CTE (10.5 ppm K⁻¹), excellent optical transparency (YI = 3.4, T_{400} = 80.8%), a very high T_g (351 °C) and solution-processability. Thus, some of the *s*-spiro- and *a*-spiro-type PEsIs developed in this work are promising candidate plastic substrates for use in image display devices and other optoelectronic materials.

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Appendix A. Supplementary data

Supplementary data related to this article can be available at

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http://www.sumitomo-chem.co.jp/sep/english/products/pes/index.html

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Table 1 The properties of PEsIs derived from TA-s-Spiro and common diamines and comparative system.

No.	Tetracarboxylic dianhydride (TCDA)	Diamine	$\eta_{\rm inh}$ (dL g ⁻¹)	Imidization method ^c	Solvent for casting (PI content)	T_{400} (%)	λ_{cut} (nm)	$T_{\rm tot}$ (%)	YI	Haze (%)	Δn_{th}	Т _g (°С)	CTE (ppm K ⁻¹)	$T_{\rm d}^{5}$ (N ₂) (°C)
1	TA-s-Spiro	4,4'-ODA	0.96 ^a 1.17 ^b	С	NMP (15 wt%)	11.6	373	82.2	23.9	13.0	0.026	292 ^e	54.1	> 550
2	TA-s-Spiro	p-PDA	1.34 ^a	Т		11.7	370	78.2	33.1	0.77	0.008	348 ^d	57.5	478
3	TA-s-Spiro	t-CHDA	0.50 ^a	Т		N	o data	because	of the	e absend	ce of fil	m-fori	ning abili	ty
4	TA-s-Spiro	DABA	1.41 ^a 0.69 ^b	С	DMAc (15 wt%)	6.4	382	87.1	26.9	15.6	0.043	362 ^d 343 ^e	39.5	432
5-1 ^f	TA-s-Spiro	TFMB	1.53 ^a 1.17 ^b	С	GBL (9.1 wt%)	48.3	367	88.2	3.7	1.90	0.037	323 ^d 340 ^e	45.6	491
Com	parative syste	ms						Y						
6 ^g	TA-Cardo	TFMB	0.67 ^a 0.68 ^b	С	GBL (9.1 wt%)	55.9	364	88.6	2.7	1.32	0.021	285 ^d	50.7	498

^a Data for PAA solutions just after polymerization.

^b Data for chemically imidized powder samples.

^c C: chemical imidization, T: thermal imidization

^d Data determined by DMA (method-1).

^e Data determined by TMA (method-2).

 ${}^{\rm f}M_{\rm w} = 1.12 \times 10^5, M_{\rm n} = 5.09 \times 10^4.$

 ${}^{g}M_{w} = 5.04 \times 10^{4}, M_{n} = 1.98 \times 10^{4}.$



TA-s-Spiro/4,4'-ODA

													/		
			NMP	DMAc	DMF	DMSO	<i>m</i> -CR	CPN	GBL	DOX	THF	CF	ACT	EtAc	TriGL
No.	TCDA	Diamine				Неа	ting ter	nperatu	re (°C)	at the 2	nd step	,	/		
			150	150	140	150	150	130	150	100	60	50	50	80	150
1	TA-s-Spiro	4,4'-ODA	++	++	++	++	++	_	++	++	++	+	_	_	++
4	ibid	DABA	++	++	++	++	++	+	++	7	_	_	_	_	++
5-1	ibid	TFMB	++	++	++	++	++	++	++	++	++	++	+	+	++
6	TA-Cardo	TFMB	++	++	++	++	++	++	++	++	++				++
7	TA-s-Spiro (50) 6FDA (50)	TFMB	++	++	++	++	+	++	++	++	++	++	+	±	++
8	TA-s-Spiro (70) PMDA (30)	TMFB	++	++	++	++	+	++	++	+	++	++	+	++	++
9	TA-s-Spiro (70) NTDA (30)	TFMB	++	++	++	++	++	++	++	_	_	_	_	+	++
10	TA-s-Spiro (60) NTDA (40)	TFMB	++	++	++	++	++	+	+	_	_	_	_	+	++
11	TA-s-Spiro (50) CBDA (50)	TFMB	++	++	++	++	++	++	++	++	++				_
12	TA-Cardo (50) CBDA (50)	TFMB	++	++	++	++	++	++	++	++	++				++

Table 2 The solubility of chemically imidized powder samples for TA-s-Spiro-based PEsIs and related systems.

(++) Soluble at room temperature, (+) soluble when heated at established temperatures and homogeneous after cooling to room temperature, (\pm) deformed or swelled, and (–) insoluble even by heating. *m*-CR = *m*-cresol, DOX = 1,4-dioxane, CF = chloroform, ACT = acetone, EtAc = ethyl acetate.

														Y		
No.	TCDA (mol%)	$\eta_{\rm inh}$ (dL g ⁻¹)	Solvent for casting (PI content)	T_{400} (%)	λ _{cut} (nm)	$T_{\rm tot}$ (%)	YI	Haze (%)	$\Delta n_{\rm th}$	Т _g (°С)	CTE (ppm K ⁻¹)	E (GPa)	σ _b (GPa)	ε _b av/max (%)	T_{d}^{5} (N ₂) (°C)	$\begin{array}{c} T_{\rm d}^{5} \\ ({\rm air}) \\ (^{\circ}{\rm C}) \end{array}$
5-1	TA-s-Spiro	1.53 ^a 1.17 ^b	GBL (9.1 wt%)	48.3	367	88.2	3.7	1.90	0.037	323 ^c 340 ^d	45.6	2.77	0.09	6.1/9.8	491	471
5-2	ibid	1.28 ^a 1.07 ^b	CPN (20 wt%)	47.8	365	87.7	5.5	0.67	0.030	315 ^c 337 ^d	45.0	3.08	0.11	6.0/9.5	519	471
7	TA-s-Spiro (50) 6FDA (50)	1.14 ^a 1.02 ^b	CPN (15 wt%)	65.7	360	89.1	3.3	0.72	0.027	310 ^c 348 ^d	52.0	3.21	0.11	7.5/11.5	493	488
8	TA-s-Spiro (70) PMDA (30)	0.85^{a} 0.46^{b}	GBL (20 wt%)	35.0	370	87.7	9.9	0.83	0.035	321 ^d	45.8				503	
9	TA-s-Spiro (70) NTDA (30)	1.52 ^a 0.99 ^b	CPN (12wt%)	49.1	381	86.4	9.1	0.66	0.047	330° 338 ^d	33.5					487
10	TA-s-Spiro (60) NTDA (40)	1.15 ^a 1.10 ^b	CPN (6 wt%)	52.4	382	86.4	6.4	1.04	0.057	320 ^d	26.1				541	
11 ^e	TA-s-Spiro (50) CBDA (50)	0.99 ^a 1.20 ^b	DMAc (7 wt%)	66.7	353	88.8	3.3	1.13	0.051	345°	29.0	5.10	0.18	6.7/9.9	452	445
Con	parative system	ms														
12	TA-Cardo (50) CBDA (50)	1.19 ^a 1.19 ^b	GBL (9.8 wt%)	65.9	358	88.6	3.6	1.36	0.035	304	39.9	3.27	0.10	5.4/9.2	461	448

Table 3 The properties of PEsIs derived from TA-s-Spiro with TFMB and related copolymers

 prepared via chemical imidization.

^a Data for PAA solutions just after polymerization.

^b Data for chemically imidized powder samples.

^c Data determined by DMA (method-1).

^d Data determined by TMA (method-2).

 $^{e}M_{w} = 8.14 \times 10^{4}, M_{n} = 3.26 \times 10^{4}.$

No.	Diamine	$\eta_{\rm inh}$ (dL g ⁻¹)	Solvent for casting (PI content)	T_{400} (%)	λ _{cut} (nm)	$T_{\rm tot}$ (%)	YI	Haze (%)	<i>T</i> _g ^c (°C)	CTE (ppm K ⁻¹)	E (GPa)	σ _b (GPa)	ε _b av/max (%)	$T_{\rm d}^{5}$ (N ₂) (°C)
12	AB-s-Spiro	1.53 ^a 1.75 ^b	CPN (8 wt%)	79.2	328	87.3	5.7	1.20	371	39.0	3.01	0.11	5.6/8.4	449
13	AB-s-Spiro (50) TFMB (50)	1.07 ^a 1.63 ^b	CPN (8 wt%)	82.8	320	87.0	3.7	2.29	364	26.0	4.63	0.17	7.2/12.2	448
Compa	arative systems													
14	AB-Cardo	1.07 ^a]	Inhomog	eneous	state du	ring chei	nical ii	midization	and imp	perfect i	midization	l
15	AB-Cardo (50) TFMB (50)	1.72 ^a 1.57 ^b	DMAc (8 wt%)	84.4	318	88.8	1.8	3.65	343	30.8	3.53	0.14	7.2/9.8	440
16	AP-s-Spiro	2.50 ^a 1.64 ^b	DMAc (7 wt%)	80.0	317	87.7	3.4	1.71	360	49.1	2.75	0.11	8.7/19.5	467
17	AP-Cardo	0.82 ^a]	Inhomog	eneous	state du	ring chei	nical in	midization a	and imp	erfect i	midization	l
18	AP-s-Spiro (50) TFMB (50)	1.85 ^a 2.24 ^b	DMAc (7.4 wt%)	77.4	317	88.1	5.0	2.18	356	39.1	3.95	0.14	8.0/11.3	449
19	AP-Cardo (50) TFMB (50)	1.30 ^a]	Inhomog	eneous	state du	ring chei	nical ii	nidization	and imp	erfect i	midization	1

Table 4 The properties of PEsIs derived from CBDA with AB-*s*-Spiro and related copolymers prepared via chemical imidization.

^a Data for PAA solutions just after polymerization.

^b Data for chemically imidized powder samples.

^c Data determined by DMA (method-1).

		NMP	DMAc	DMF	DMSO	<i>m</i> -CR	CPN	GBL	DOX	THF	TriGL
No.	Diamine			Hea	ating temp	erature (°	°C) at the	2nd ste	p	2	7
		150	150	140	150	150	130	150	100	60	150
12	AB-s-Spiro	++	++	++	++	+	++	++		_	_
13	AB-s-Spiro (50) TFMB (50)	++	++	++	++	+	++	+) -	+	_
15	AB-Cardo (50) TFMB (50)	++	++	++	++	_	Ż	++	_	_	_
16	AP-s-Spiro	++	++	++	++	- /		_	_	_	_
18	AP-s-Spiro (50) TFMB (50)	+	+	+	±			+	_	_	_

Table 5 The solubility of chemically imidized powder samples for PEsIs derived from CBDA with AB-*s*-Spiro and related systems.

(++) Soluble at room temperature, (+) soluble when heated at established temperatures and homogeneous after cooling to room temperature, (\pm) deformed or swelled, and (-) insoluble even by heating.

m-CR = m-cresol, DOX = 1,4-dioxane, CF = chloroform, ACT = acetone, EtAc = ethyl acetate.

No.	Tetracarboxylic dianhydride	Diamine	$\eta_{\rm inh}$ (dL g ⁻¹)	Imidization method ^c	Solvent for casting (PI content)	T_{400} (%)	λ_{cut} (nm)	T_{tot} (%)	YI	Haze (%)	$\Delta n_{\rm th}$	<i>T</i> _g (°C)	CTE (ppm K ⁻¹)	T_{d}^{5} (N ₂) (°C)
20	TA-a-Spiro	4,4'-ODA	1.09 ^a 1.43 ^b	С	DMAc (15 wt%)	3.1	387	83.8	26.8	2.44	0.022	270 ^d 293 ^e	37.3	478
21	TA-a-Spiro	p-PDA	2.05 ^a	Т		1.8	392	78.2	68.3	2.81	0.013	298 ^d	48.3	
22	TA-a-Spiro	t-CHDA	1.01 ^a	Т		N	lo data	because	e of the	absend	ce of fil	m-form	ning abilit	y
23	TA-a-Spiro	TFMB	1.48 ^a 1.85 ^b	С	CPN (15wt%)	28.9	371	85.4	11.7	2.09	0.059	268 ^d 290 ^e	25.4	499
24	TA- <i>a</i> -Spiro (50) 6FDA (50)	TFMB	1.15 ^a 1.41 ^b	С	CPN (15wt%)	46.6	362	88.4	5.9	0.77	0.042	289 ^d 331 ^e	41.7	510

Table 6 The properties of PEsIs derived from TA-*a*-Spiro with common diamines and related copolymer.

^a Data for PAA solutions just after polymerization.

^b Data for chemically imidized powder samples.

^c C: chemical imidization, T: thermal imidization

^d Data determined by DMA (method-1).

^e Data determined by TMA (method-2).

Table	7	The	solubility	of	chemically	imidized	powder	samples	for	PEsIs	derived	from
asymn	netr	ic Sp	iro-type mo	onor	ners.							

			NMP	DMAc	DMF	DMSO	<i>m</i> -CR	CPN	GBL	DOX	THF	CF	ACT	EtAc	TriGL
No.	TCDA	Diamine				Hea	ating ter	nperatu	re (°C)	at the 2	nd step	р			
			150	150	140	150	150	130	150	100	60	50	50	80	150
20	TA-a-Spiro	4,4'-ODA	++	++	++	+	+	+	+	+) +	++	_	_	_
23	TA-a-Spiro	TFMB	++	++	++	++	+	++	+	++	++	+	_	_	+
24	TA- <i>a</i> -Spiro (50) 6FDA (50)	TFMB	++	++	++	++	+	++	++	++	++	++	+	±	++
25	CBDA	AB-a-Spiro	++	++	+	±	-	±	±	_	_	_	_	_	_
26 ^a	CBDA	AB- <i>a</i> -Spiro (50) TFMB (50)	++	++	++	++	+	+	+	_	_	_	_	_	_
28	6FDA	TFMB	++	++	++	++	+	, ++	++	++	++	++	++	++	++

(++) Soluble at room temperature, (+) soluble when heated at established temperatures and homogeneous after cooling to room temperature, (±) deformed or swelled, and (–) insoluble even by heating. ^a Sample with a η_{inh} of 1.09 dL g⁻¹.

m-CR = m-cresol, DOX = 1,4-dioxane, CF = chloroform, ACT = acetone, EtAc = ethyl acetate.

No.	Diamine	$\eta_{\rm inh}$ (dL g ⁻¹)	Imidization method ^c	Solvent for casting (PI content)	T_{400} (%)	λ _{cut} (nm)	$T_{ m tot}$ (%)	YI	Haze (%)	Т _g (°С)	CTE (ppm K ⁻¹)	E (GPa)	σ _b (GPa)	ε _b av/max (%)	$T_{\rm d}^{5}$ (N ₂) (°C)
25	AB-a-Spiro	0.94 ^a 0.91 ^b	С	DMAc (10 wt%)	83.8	329	88.2	1.7	0.81	d	^d	d	d	d	
26	AB- <i>a</i> -Spiro (50) TFMB (50)	2.38 ^a 6.92 ^b	С	DMAc (10 wt%)	80.8	320	87.7	3.4	2.81	351 ^e 372 ^f	10.5 (17.9) ^g	6.12 ^h	0.15 ^h	3.7/6.0 ^h	440
27	AB- <i>a</i> -Spiro (40) TFMB (60)	2.92 ^a 6.77 ^b	С	DMAc (10 wt%)	81.7	315	88.2	3.1	1.82	389 ^f	9.8	1			
Compa	arative system														

89.8

4.0

Table 8 The properties of PEsIs derived from CBDA with AB-a-Spiro and related copolymer.

^a Data for PAA solutions just after polymerization.

^b Data for chemically imidized powder samples.

Т

^c C: chemical imidization, T: thermal imidization

^d The measurements were disturbed by film brittleness.

^e Data determined by DMA (method-1).

1.63^a

28

TFMB

^fData determined by TMA (method-2).

^g Data for the sample with a η_{inh} of 1.09 dL g⁻¹.

^h Mechanical data averaged for the specimens of n = 7 (only for sample # 26).

84.2

302



6.43

0.19 3.2/6.0

444

22.9

0.87 345°

Appearance of PEsI film (#26)



Fig. 1. CTE and solubility of two types of *t*-CHDA-based transparent PI films prepared via the conventional two-step process and the steric substructure of fluorene-pendant cardo moiety (CS Chem3D Pro, MOPAC).



Fig. 2. The reaction schemes for the synthesis of symmetric and asymmetric spiro-type fluorene-pendant bisphenols (*s*- and *a*-Spiro-FLBP) and the steric substructure of fluorene-pendant spiro moiety introduced in PI main chains (CS Chem3D Pro).



Fig. 3. The reaction schemes for the synthesis of ester-linked spiro-type and cardo-type monomers: (a) tetracarboxylic dianhydrides and (b) diamines.



Fig. 4. The chemical structures of common monomers used in this study and the steric structure of CBDA (*trans*-form).





Fig. 5. The reaction schemes for polyaddition and imidization and PI film preparation processes based on different imidization methods: (a) Chemical imidization and (b) thermal imidization.



Fig. 6. ¹H-NMR spectrum (in DMSO- d_6) of the chemically imidized PEsI derived from TA-*s*-Spiro and TFMB.



Fig. 7. Comparisons of the properties between cardo (*X*-axis) and spiro systems (*Y*-axis): (a) T_g , (b) CTE, and (c) T_{400} . Open symbols: AB-Cardo systems vs. AB-*s*-Spiro systems, closed symbols: TA-Cardo systems vs. TA-*s*-Spiro systems. The dotted lines denote the Y = X line.



Fig. 8. Main chain linearity of *a*-spiro-type PEsIs: (a) TA-*a*-Spiro/TFMB and (b)

CBDA/AB-a-Spiro systems.



Fig. 9. Comparisons of the properties for symmetric (*X*-axis) and asymmetric (*Y*-axis) spiro-type systems: (a) T_g , (b) CTE, and (c) T_{400} . Open and closed symbols are for AB-Spiro-based and TA-Spiro-based PEsI systems, respectively. The dotted lines denote the Y = X line.
Highlights

- ► This work proposes novel symmetric and asymmetric spiro-type poly(ester imide)s (PEsIs).
- ► The chemically imidized PEsIs were highly soluble even in less hygroscopic solvents.
- Solution casting provided colorless films with a very low CTE and a very high T_g . The

PEsIs obtained are useful as novel high-temperature plastic substrates in display devices.

Chilling Marker