

Poly(ester imide)s derived from Trimellitic Anhydride

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Abstract: The synthesis and film properties of polyimides containing ester linkages in the main chains are discussed in this study. The ester-containing dianhydride monomers were synthesized from various diols and trimellitic anhydride. First, the dianhydride from hydroquinone or 4,4'-biphenol was reacted with *p*-phenylenediamine in DMAc, and high molecular weight poly(amic acid)s (PAAs) were obtained. These tough PI films prepared under optimum cure conditions showed considerably low CTE values (< 10 ppm/K), indicating that the para-ester linkage behaves as a rigid-rod unit favorable for the spontaneous in-plane orientation. However, these were insoluble in any organic solvents. On the other hand, the use of the dianhydride from 2,2'-biphenol gave PIs possessing high thermoplasticity, high solubility in NMP, and high T_g's (> 240°C), simultaneously. This results from the bent and distorted structure at the 2,2'-biphenyl unit, where the internal rotation is restricted.

1. Introduction

We have studied the low CTE generation mechanism in polyimide (PI) systems and revealed that the polyimide chain stiffness/linearity plays a very important role for the thermal imidization-induced in-plane molecular orientation related closely to the CTE values [1]. Para-amide linkages, which has a double bond character through the keto-enol tautomerism, are also classified into a category of a rigid/linear structural unit desirable for low CTE. In fact, polyimides (PIs) derived from 4,4'-diaminobenzanilide (DABA), e.g., PMDA/DABA and s-BPDA/DABA (PMDA = pyromellitic dianhydride, s-BPDA = 3,3',4,4'-biphenyl tetracarboxylic dianhydride) show considerably low CTE values. On the other hand, there are no reports describing how the introduction of para-ester linkages into PI main chains contributes to the in-plane orientation during thermal imidization. This is our first motivation of the present work. In this paper, para-ester linkages were introduced by using an ester-containing dianhydride monomer derived from trimellitic anhydride (TMA_n) and various diols since TMA_n is a very cheap commercially available chemical and it is possible to prepare various functional poly(ester imide) (PEI) for desired structural modifications. The present study describes that, depending on the diols structure used for dianhydride synthesis, PEIs displayed a low CTE characteristics and a high processability.

2. Experimental Section

Ester-containing dianhydride monomers were prepared from some diols (hydroquinone, 4,4'-biphenol, 2,2'-biphenol, and others) and trimellitic anhydride chloride in THF or DMF in the presence of pyridine as a HCl-acceptor at room temperature as shown in Fig.1. The crude ester-containing dianhydrides obtained were repeatedly recrystallized from adequate solvents then vacuum-dried at 120–200°C. PEI precursors were polymerized in the common procedure

in DMAc at room temperature for 24–48 h using the diamines listed in Fig.1. High molecular weights of PEI precursors were readily obtained. The inherent viscosities measured at 0.5 wt% in DMAc at 30°C ranged from 0.30 to 5.2 dL/g. The PEI precursor solutions were cast at 60°C/2h on a glass plate. The cast films were all flexible. The precursor films were imidized at 250°C/2h + 300°C/1h on a substrate then annealed at an established temperature (310°C for non-thermoplastic PEIs, and $T_g - 5^\circ\text{C}$ for thermoplastic PEIs to avoid film deformation) for 1 h in a free-standing state to remove residual stress. Complete imidization was confirmed from the infrared spectra.

The CTEs of the PI specimens (10 mm long, 5 mm wide, and typically 10 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 (Mac Science TMA 4010) with a load (0.5 g per film thickness in μm) in a nitrogen flow. Storage modulus (E') and loss energy (E'') were measured as a function of temperature to determine T_g from a peak temperature of the E'' curve using the same instrument at a heating rate of 5°C/min with a sinusoidal load frequency of 0.1 Hz in a nitrogen atmosphere. Thermogravimetric analysis (TGA) was conducted to evaluate the thermal stability of PI films at a heating rate of 10°C/min in nitrogen and air. The 5 % weight loss temperatures (T_d^5) were compared. The in-plane (n_{in}) and out-of-plane (n_{out}) refractive indices of PI films were measured at D-line (538.9 nm) on an Abbe refractometer (Atago 4T) equipped with a polarizer using a contact liquid (sulfur-saturated methylene iodide $n_D = 1.78\text{--}1.80$) and a test piece ($n_D = 1.92$). The average refractive index was calculated from the relation: $n_{\text{av}} = (2 n_{\text{in}} + n_{\text{out}})/3$. Dielectric constants (K_{RI}) of PEI films were estimated from a relation: $K_{\text{RI}} = 1.1 n_{\text{av}}^2$.

3. Results and Discussion

The dianhydrides derived from hydroquinone (HQ) showed high polymerization reactivity with various aromatic diamines as listed in Table 1. When trans-1,4-cyclohexanediamine (CHDA) was used as a diamine component, salt formation was observed at the initial reaction

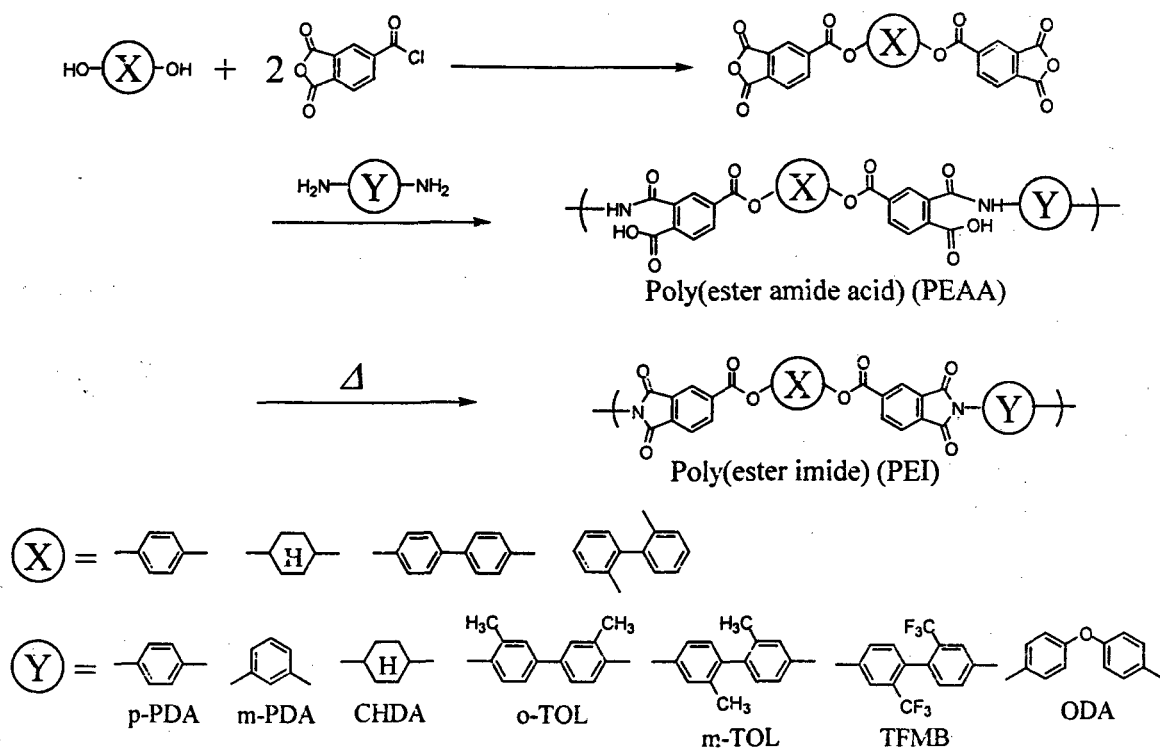


Fig.1 Synthetic route of poly(ester imide)s and structures of monomers used.

stage, but polymerization was allowed to proceed at room temperature via gradual salt dissolution during a prolonged stirring. Thermal imidization of HQ-based PEI precursors led to highly tough films. It should be noted that the HQ-based PEI using p-phenylenediamine (p-PDA) as a diamine component, (No.1), displayed an extremely low CTE (3.2 ppm/K) comparable to the value of silicone substrate. Other HQ-based PEIs also showed low CTE characteristics (CTE = 18 ppm/K for PEI from CHDA (No.2), which is comparable to copper substrate, and 31.5 ppm/K for PEI from TFMB (No.3), and 7.7 ppm/K for PEI from DABA (No.4)). The results revealed that the para-ester linkages behave as a stiff/linear structural unit like para-aramide linkages, favorable for the thermal imidization-induced in-plane orientation, which lowers CTE. No clear glass transitions were observed for the low-CTE PEIs (No. 1, 2, and 4) in the DMTA curves (20–400°C), suggesting that these PEIs with stiff/linear chain structures are probably semi-crystalline. These low-CTE PEI films were insoluble in any common organic solvents. A similar trend was observed in 4,4'-biphenol-based PEI using p-PDA. The PEIs (No.2 and 4) have another feature, high transparency.

We have previously reported the film properties of PIs derived from biphenyltetracarboxylic dianhydride (BPDA) isomers, [2,3] and revealed that a bent/distorted steric structure of PIs from 2,3,3',4'- and 2,2',3,3'-BPDA exhibited always higher Tg's than the corresponding PIs from a symmetric structure of 3,3',4,4'-BPDA. The results can be rationalized in terms of the restricted internal rotation around the biphenyl linkages in 2,3,3',4'- and 2,2',3,3'-BPDA. On the basis of the results, in the present work, we studied the isomer effect on the PEI film properties in a comparison between 4,4'-biphenol- and 2,2'-biphenol-based PEIs.

As shown in Table 1, 2,2'-biphenol-based dianhydride was apparently less reactive with diamines than 4,4'-biphenol-based one. This may include, in addition to its intrinsic lower reactivity, a contribution due to a lower purity (crystallinity) of 2,2'-biphenol-based dianhydride in contrast to the fact that 4,4'-biphenol-based dianhydride is well recrystallized for high purification. Nonetheless, the as cast PEI precursors and their imidized films were flexible. The 2,2'-biphenol-derived PEI using p-PDA (No.6) showed a high Tg at 243°C. The E' curve in DMTA decreased abruptly above the Tg, indicating that this PEI is highly thermoplastic. A hot plate test at 350°C suggested its very high melt flowability comparable to that of a typical thermoplastic poly(ether imide), injection-moldable ULTEM 1000 (melt viscosity is ca. 3000 poise at 350°C). Another prominent property is the solubility; this PEI can be dissolved in NMP even at a very high concentration (> 20 wt%). The PEI using o-tolidine (o-TOL) (No.7) also showed excellent thermo-and solution-processability.

Table 1 Film Properties of typical Poly(ester imide)s.

No.	Diol (X)	Diamine (Y)	[η] (dL/g)	Tg (°C)	CTE (ppm/K)	solubility
1	hydroquinone	p-PDA	5.19	not detected	3.2	0
2	hydroquinone	CHDA	0.52	----	18.0	0
3	hydroquinone	TFMB	2.93	> 360	31.5	0
4	hydroquinone	DABA	2.37	not detected	7.7	0
5	4,4'-biphenol	p-PDA	1.12	not detected	7.4	0
6	2,2'-biphenol	p-PDA	0.43	243	66.3	22.6
7	2,2'-biphenol	o-TOL	0.30	253	75.6	21.1

参考文献 [1] M.Hasegawa et al., *Macromol.*, **29**, 7897 (1996), [2] M.Hasegawa, *Macromol.*, **32**, 387 (1999), [3] M.Hasegawa, *Abstract of 4th China-Japan Seminar on Advanced Aromatic Polymers*, 2001, Tokyo