



Solution-processable transparent polyimides with low coefficients of thermal expansion and self-orientation behavior induced by solution casting



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ARTICLE INFO

Article history:

Received 25 May 2013

Accepted 7 August 2013

Available online 19 August 2013

Keywords:

Transparent polyimide

Thermal expansion

Self-orientation

Solution processability

Heat-resistant plastic substrates

ABSTRACT

A fluorinated tetracarboxylic dianhydride (amide-type TA-TFMB) was prepared from trimellitic anhydride chloride and 2,2'-bis(trifluoromethyl)benzidine (TFMB). A chemically imidized polyimide (PI) derived from TA-TFMB and TFMB was rather soluble in various solvents. Solution casting of this PI (TA-TFMB/TFMB) led to a flexible, non-turbid, and seemingly almost colorless PI film with a high T_g of 328 °C and a considerably low coefficient of thermal expansion (CTE) of 9.9 ppm K⁻¹ which results from significant in-plane chain orientation induced during solution casting. The self-orientation mechanism is discussed. The properties of TA-TFMB/TFMB were compared with those of some relevant systems. The results suggest that an electron-withdrawing effect of the 2,2'-CF₃ substituents of TA-TFMB and a twisted conformation of the central biphenyl moiety greatly contribute to the suppressed coloration of the TA-TFMB/TFMB film. The use of a TA-TFMB counterpart (ester-type TA-TFBP) was effective for further enhancing the transparency owing to reduced charge-transfer interaction. However, the thermal properties of TA-TFBP/TFMB were not always satisfactory. Copolymerization using 2,3,6,7-naphthalenetetracarboxylic dianhydride led to a PI film with an increased T_g of 277 °C and a very low CTE of 12.6 ppm K⁻¹ without significant decreases in the transparency and the solubility. Thus, this work proposes promising candidates as novel heat-resistant plastic substrate materials in display devices.

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1. Introduction

Optically transparent high-temperature polymers are prospective materials for various optoelectronic applications. A recent urgent subject is to develop transparent plastic substrate materials alternative to fragile/heavy inorganic glass substrates. The plastic substrates are required to simultaneously possess outstanding heat resistance ($T_g > 250$ °C, more desirably >300 °C) and excellent dimensional stability for overcoming some thermal processes in device fabrication. The direct strategy for enhancing the dimensional stability is to reduce the linear coefficients of

thermal expansion (CTE) with a perfect isotropy within the film plane (X – Y) direction, which is difficult to realize it by mechanical stretching. The combined properties of high T_g ($> \sim 300$ °C) and XY -isotropically low CTE ($< \sim 20$ ppm K⁻¹) are observed in some aromatic polyimide (PI) systems only when the backbone structures are highly linear/stiff [1–3]. The suppressed thermal expansion behavior is closely related to a high level of the main chain orientation along to the X – Y direction (called in-plane orientation), which occurs during cyclodehydration (thermal imidization) of the PI precursor cast films [4,5]. Aromatic PIs are most reliable heat-resistant polymers used in electric and microelectronic applications for the absence of volatile organic compounds and metallic/ionic contaminations, non-flammability, thermo-oxidative stability, and good

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mechanical properties [6–17]. However, originally intensive coloration of conventional aromatic PI films, which is based on charge-transfer (CT) interactions arising from the electron donor–acceptor alternating chain sequences [18], often disturbs their optical applications. So far, much effort has been devoted to erase PI film coloration from academic and industrial interests. The most effective strategy for inhibiting CT interactions is to use non-aromatic (cycloaliphatic) monomers either in diamines or tetracarboxylic dianhydrides or both [19–25]. However, most of cycloaliphatic monomers negatively contribute to low CTE generation owing to their non-linear/non-planar steric structures except for 1,2,3,4-cyclobutanetetracarboxylic dianhydride (CBDA) and *trans*-1,4-cyclohexanediamine (t-CHDA). Semi-cycloaliphatic PI systems, i.e., CBDA/TFMB [TFMB = 2,2'-bis(trifluoromethyl)benzidine] and s-BPDA/t-CHDA (s-BPDA = 3,3',4,4'-biphenyltetracarboxylic dianhydride) are rare cases simultaneously showing high T_g , low CTE, and high transparency [26,27]. However, these systems are essentially insoluble in common solvents, thus indicating the absence of solution-processability using the imidized form. We recently revealed that an optically transparent PI film prepared by casting (coating/drying) from the PI solution tends to give rise to lower CTE than those of the counterpart prepared upon thermal imidization of the corresponding PI precursor cast film [28]. The resultant lower CTE is attributed to a sort of “self-orientation” behavior of the PI chains during the solvent evaporation process. The present work describes a molecular design for realizing low CTE (temporary, $<15 \text{ ppm K}^{-1}$) by such casting-induced self-orientation while keeping high optical transparency and high T_g and discusses the resultant film properties.

2. Experimental

2.1. Materials

2.1.1. Monomer synthesis

An amide-type CF_3 -containing tetracarboxylic dianhydride (TA-TFMB) was synthesized according to a reaction

scheme shown in Fig. 1(a); trimellitic anhydride chloride [TMAC, 20 mmol, Tokyo Chemical Industry (TCI)] was dissolved in an anhydrous mixed solvent of ethyl acetate (14 mL) and *n*-hexane (20 mL) in a sealed flask with a septum cap. In a separate sealed flask, TFMB (5 mmol, Wakayama Seika) was dissolved in the mixed solvent (14 mL) in the presence of 0.7 mL propylene oxide (PO, 10 mmol) as an HCl acceptor. The TFMB solution was slowly added to the TMAC solution cooled at -20°C in an ethanol/ice bath over 3 h using a syringe with continuous magnetic stirring, and the reaction mixture was additionally stirred at room temperature for 12 h. The white precipitate formed was collected by filtration, washed with the mixed solvent, and vacuum-dried at 120°C for 12 h (yield: 81%). The crude product was purified by recrystallization from an acetic anhydride (Ac_2O)/toluene mixture (1/10, v/v) and dried at 120°C in vacuum for 12 h. The product showed a sharp melting peak at 274°C by the differential scanning calorimetry (DSC, Bruker-AXS, DSC3100) conducted at a heating rate of 5 K min^{-1} . The molecular structure of the product was confirmed to be the desired compound (TA-TFMB) from FTIR (JASCO, FT-IR 5300) and ^1H NMR (JEOL, JNM-ECP400) spectra, and elemental analysis. FTIR (KBr, cm^{-1}): 3310 (amide N–H), 3192/3119/3067 ($\text{C}_{\text{arom}}\text{--H}$), 1858/1777 (acid anhydride C=O), 1659/1528 (amide C=O), 1489 (1,4-phenylene), 1327 (C–F). ^1H NMR [400 MHz, dimethyl sulfoxide (DMSO)- d_6 , δ , ppm]: 11.06 (s, 2H, amide), 8.66 (s, 2H, 3,3'-protons of phthalimide), 8.53 (d, 2H, 5,5'-protons of phthalimide, $J = 7.9 \text{ Hz}$), 8.37 (s, 2H, 3,3'-protons of biphenyl), 8.28 (d, 2H, 6,6'-protons of phthalimide, $J = 7.8 \text{ Hz}$), 8.15 (d, 2H, 5,5'-protons of biphenyl, $J = 8.5 \text{ Hz}$), 7.45 (d, 2H, 6,6'-protons of biphenyl, $J = 8.4 \text{ Hz}$). HRMS-EI: m/z (M^+) calcd. for $\text{C}_{32}\text{H}_{14}\text{O}_8\text{N}_2\text{F}_6$ (668.0655), Found: 668.0654.

A TA-TFMB isomer derived from 3,3'-bis(trifluoromethyl)benzidine and TMAC, i.e., TA-33TFMB (pale-yellow powder) was also synthesized in a similar manner. FTIR (KBr, cm^{-1}): 3279 (amide N–H), 3110 ($\text{C}_{\text{arom}}\text{--H}$), 1858/1775 (acid anhydride C=O), 1659/1564 (amide C=O), 1356 (C–F). ^1H NMR [400 MHz, DMSO - d_6 , δ , ppm]: 10.79 (s, 2H, amide), 8.58 (s, 2H, 3,3'-protons of phthalimide), 8.50 (d, 2H, 6,6'-protons of phthalimide, $J = 8.0 \text{ Hz}$), 8.27

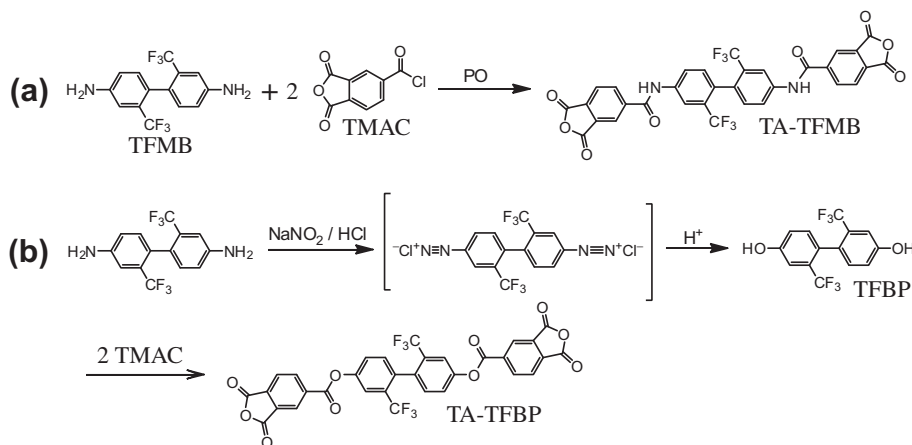


Fig. 1. Reaction schemes for syntheses of CF_3 -containing tetracarboxylic dianhydrides: (a) amide type and (b) ester type.

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