# Characterization of fluorinated polyimide morphology by transition mechanical analysis

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## ARTICLE INFO

## ABSTRACT

We report the thermal transition and concomitant morphology change of polyimide films, investigated through dynamic mechanical analyses, thermo-mechanical analyses, and X-ray diffraction spectroscopy. For this study, highly transparent polyimide films composed of 3,4,3′,4′-biphenyltetracarboxylic dianhydride and fluorinated diamines, 2,2′-bis(trifluoromethyl)-4,4′-diaminobiphenyl, are prepared through a solvent-casting method. The films are annealed at different temperatures, and two kinds of reaction solvents (n-methyl-2-pyrrolidone and N,N-dimethylacetamide) for the polyimide precursors are compared. The mechanical analyses during thermal transition along with spectroscopic measurements reveal unusual transition behaviors and morphology differences between the polyimide films at various annealing temperatures. The results can be applied to the quantitative analysis of the imidization ratio in highly imidized polyimides when the films are imidized thermally at temperatures above 300 °C.

## 1. Introduction

Lightness and better portability are the most desired features in current mobile display devices [1–5]. However, the most widely used glass substrates in such devices lack lightness, flexibility, and thinness, which are necessary features for display technologies in the near future. Furthermore, the fragile nature of glass substrates means they have low durability, despite recent improvements in the impact strength of tempered glass [4,5]. Therefore, it is necessary to develop flexible plastic substrates with thermal and optical properties as good as those found in inorganic substrates such as glass or silicon wafer, in order to utilize the other various advantages they can provide [6–8].

For application in electronic devices, a high-temperature fabrication process is generally required to obtain high reliability in the manufacturing process. Such process conditions mean that common transparent plastics such as polyethylene naphthalates, poly(ethylene terephthalate), poly(ether sulfones), and polycarbonates are less suitable for these devices [7,8]. In contrast, the thermal stability of polyimide films probably makes them the most promising candidate substrates for the future electronic devices [7–10]. In particular, the recent marked decrease in the problem of their yellowish color as well as their well-known properties such as light weight, flexibility, and chemical inertness further increases their applicability [11–17].

The well-known charge-transfer complex (CTC) formations are lessened markedly in polyimides with fluorinated functional groups, which weaken their intra- or inter-molecular interactions. In 2005, The DuPont company patented fluorinated polyimides composed of two dianhydrides, 3,4,3′,4′-biphenyltetracarboxylic dianhydride (BPDA) and 2,2′-bis(3,4-dicarboxyphenyl)-hexafluoropropane dianhydride (6FDA), and a diamine, 2,2′-bis(trifluoromethyl)-4,4′-diaminobiphenyl (TFDB) [11]. Here, 6FDA, with its bulky trifluoro side groups, enhances transparency but reduces thermal stability [11,12]. Also, the fluorinated side groups in 6FDA and TFDB give the materials an unusual thermo-mechanical behavior that originates from moderate CTC formation and imidization [12–17]. These internal molecular re-organizations are known to make quantitative analyses difficult. In particular, when the heating temperature is higher than ≈300 °C, estimation of the degree of imidization is difficult [18–23]. The application of organic materials or polymers to electronic devices needs comparable

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thermal and chemical stabilities equivalent to those of inorganic materials, especially in terms of impurities generated through device operation. This requirement is related to the device's reliability and lifetime. In this regard, study of the dependence of polymer morphology on process conditions, such as thermal transition behavior and degree of imidization (DoI) in polyimides, is critical for determining the appropriate process conditions for organic materials.

Herein, we report the thermal transition behavior, structural change during imidization, and CTC formation in a fluorinated polyimide (FPI), the chemical structure of which is shown in Fig. 1a, with different solvents and with various curing temperatures. Along with X-ray diffraction measurements, the dependences of the thermal behaviors on the change in polymer morphology are revealed through transition mechanical analyses, which denote dynamic and mechanical analyses during thermal transition [24–27]. The change in molecular packing structure correlated to resistance strengths obtained through transition mechanical analyses provides distinguishable information on CTC formation and imidization, even in a highly imidized film. Also, the amount of residual solvent according to the annealing temperature is measured for two solvents commonly used for polyimide film fabrication, that is, N-methyl-2-pyrrolidone (NMP) and N,N-dimethylacetamide (DMAc), to determine the solvent effect on the thermal behavior of polyimide films.

## 2. Experimental

### 2.1. Polymer solution preparation

Polyimide precursor solutions (15 wt-%) were prepared from BPDA (Fig. 1b) and TFDB (Fig. 1c) in NMP (Fig. 1d) or DMAc (Fig. 1e). The solvents and monomers were purchased from Sigma Aldrich Co. BPDA ($\approx 5.2$ g) ($\approx 4.7$ g for DMAc) was agitated in a 250 mL round-bottomed flask in the presence of NMP or DMAc (60 mL) for about 1 h at 0 °C and for a further 5 h at 25 °C. Subsequently, TFDB



**Fig. 1.** (a) Fluorinated polyimide, (b) 3,4,3′,4′-biphenyltetracarboxylic dianhydride (BPDA), (c) 2,2′-bis(trifluoromethyl)-4,4′-diaminobiphenyl (TFDB), and (d) N-methyl-2-pyrolidone (NMP), (e) N,N-dimethylacetamide (DMAc).

($\approx 5.7$ g) ($\approx 5.2$ g for DMAc) was added, and the solution was stirred for 17 h. All the reactions were controlled by the reflux method under a regulated $N_2$ purge to maintain the concentration of the reaction solution.

### 2.2. Film fabrication

As introduced in a previous report [13], a flow-coating technique was employed to prepare two series of five films of homogeneous thickness. One series was fabricated from NMP solution and the other from DMAc solution. The poly(amic acid) (PAA) polymer solutions were applied to glass substrates temporarily adhered to a custom-built, motorized translation stage. The film thickness was controlled by adjusting the lip gap of a metal blade to $\approx 300$ μm. After casting of the solution, the heating stage was set to 50 °C for 1 h for leveling, and 80 °C for 1 h to remove the solvent under a $N_2$ flow. The films on the glass substrates were released with initiation of the removal at one edge of the film with a razor blade, and then fixed into a square-shaped metal frame to expose both sides of the film. Finally, the films in tenter frames were thermally heated up to 300, 350, 380, 400, 430, and 450 °C in each series of solvent at a ramping rate of 2 °C/min under a $N_2$ purge. The thermally cured film thickness was in the range 45–55 μm.

### 2.3. Thermal and chemical analyses

The amount of residual solvent and the evaporation rate of the solvent were measured with a TA Instruments TGA Q5000IR. The amount of water generated during imidization and the amount of residual solvent according to heating temperature were also measured with an Agilent GC–MS 6890/5973 system with a pyrolyzer and UA-1 Column. The sample was heated from 80 °C to 500 °C at a heating rate of 10 °C/min under a He flow. A TA Instruments DSC Q2000 was used to trace the thermal curing of the films, and the heating and cooling cycles were repeated to test for reversibility. Both the TGA and DSC measurements were performed with ramping rate of 10 °C/min under a $N_2$ purge. Chemical curing was also analyzed with a Bio Rad FTS-6000 Fourier-transform IR (FTIR) spectrometer.

### 2.4. Spectroscopic methods

Optical properties such as the yellow index (YI) and UV-Vis absorption intensity (AI) were measured with a CM3600D spectrophotometer manufactured by KONICA MINOLTA Inc. XRD measurements were conducted using a laboratory-scale wide-angle X-ray scattering instrument (Philips Xpert) with Cu K$_\alpha$ radiation in the conventional pinhole geometry. The samples were mounted in the specular geometry. The Incidence angle of the 40 KeV/40 mA powered X-ray was fixed, and a diffraction pattern was obtained through a detector ($2\theta$) scan. The optical retardation was derived from the difference between the in-plane and out-of-plane refractive index of the film, as measured with a METRICON Prism coupler 200P-1 equipped with a He–Ne laser source with a wavelength of 632.8 nm.

### 2.5. Thermo-dynamic mechanical analyses

Films cut into rectangular shapes of around 5 mm × 20 mm were used for DMA and TMA measurements. TA Instruments DMA Q800 and TMA Q400 were used for the investigation of the transition behavior and the evaluation of thermal strain, respectively. In DMA measurements, a strain of 0.1% and 1 Hz oscillation were used for measuring the storage and loss modulus change as a function of temperature. Samples were sc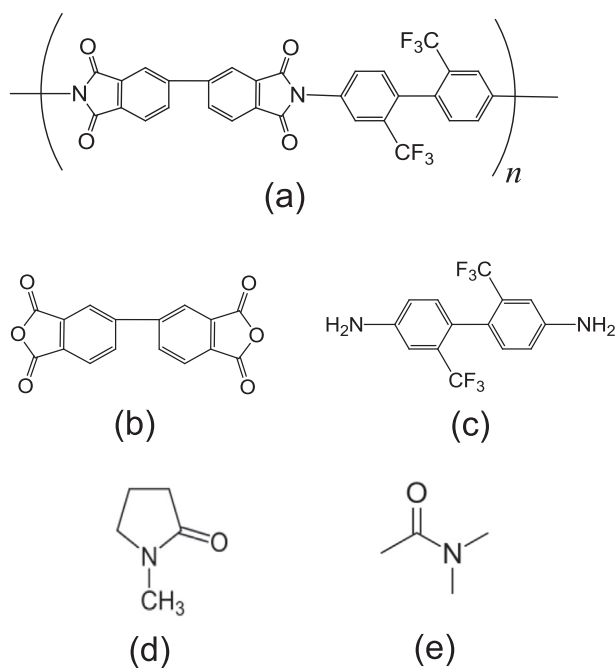anned up to 400 °C at a heating rate