

Semi-aromatic Polyimides with Both Low Dielectric Constant and Low CTE

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Abstract

This paper describes semi-aromatic polyimides possessing low dielectric constant (ϵ), low linear coefficient of thermal expansion (CTE), and high Tg. A candidate is semirigid s-BPDA-CHDA. A high molecular weight of this PI precursor was prepared under a selected condition. The thermally cured PI film was sufficiently flexible and showed a low ϵ and a comparatively low CTE, concurrently with high transparency and a high Tg. In this work, another promising candidate, CBDA-TFDB, is also discussed. The dependence of the various properties on cure conditions and film thickness are also shown.

Introduction

Much efforts for decreasing dielectric constant (ϵ) of polyimide (PI) interlayer dielectrics have been done to enhance the signal propagation rate in microprocessors. In multilayered LSI fabrication, PIs as interlayer insulators are also strongly demanded to have not only low ϵ but also low linear coefficient of thermal expansion (desirably CTE < 10 ppm/K), which reduces the residual stress and consequently dissolves some serious troubles such as delamination, curling, and film cracking in PI/metal laminates. However, the molecular design for

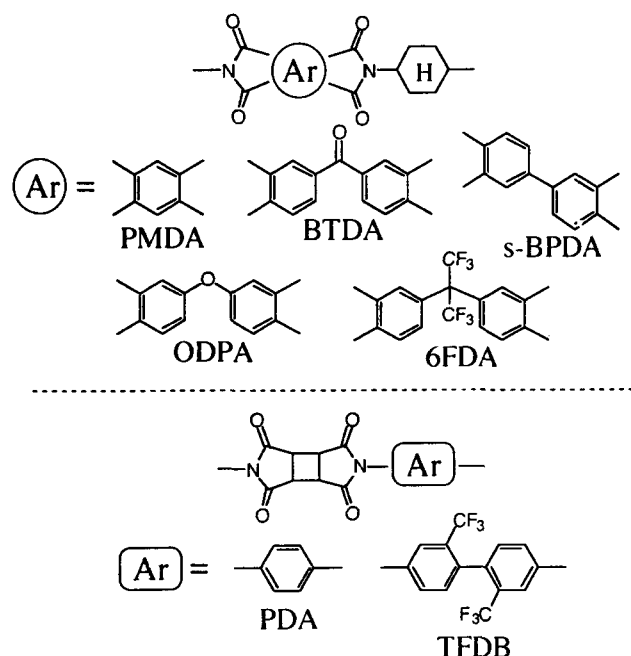


Fig.1 Structures of PIs studied.

realizing low CTE and low ϵ simultaneously is not so easy. In fact, most of low ϵ PI materials reported so far possess high CTE values (> 50 ppm/K). This paper describes an attempt to obtain the target PI materials.

Experiments

Materials. A series of semi-aromatic poly(amic acid)s (PAA) were polymerized from various aromatic dianhydrides (PMDA, *s*-BPDA, BTDA, OPA, and 6FDA) with trans-1,4-cyclohexanediamine (CHDA). The monomers used were purified by recrystallization and then vacuum-dried at suitable temperatures. Solvents for polymerization were dried with molecular sieves 4A. To obtain high molecular weight PAAs, the effects of monomer-feeding procedure (addition of dianhydride powder to diamine solution or the opposite way), kind of solvent, reaction temperature, addition of a salt (LiCl) were examined. Another series of PIs were prepared from cyclobutanetetracarboxylic dianhydride (CBDA) with *p*-phenylenediamine (PDA) or 2,2'-bis(trifluoromethyl)-4,4'-diaminobiphenyl (TFDB) on the common procedure. PI films were prepared by thermal imidization of as-cast PAA films at established temperatures on a glass substrate or in a free-standing state.

Measurements. CTEs in the in-plane direction for PI film specimens were measured on a thermomechanical analyzer (Mac Science, TMA 4000) at a heating rate of $5^{\circ}\text{C}/\text{min}$ with a load of $0.5\text{g}/1\mu\text{m}$ -film thickness. Tg's of PIs were measured by dynamic mechanical thermal analysis (DMTA) on the same apparatus at a sinusoidal load frequency of 0.1 Hz in a nitrogen atmosphere. Thermogravimetric analysis (TGA) was performed to estimate the thermal stability of PIs under a nitrogen or air flow. Dielectric constants (ϵ) were estimated from average refractive indices (n_{av}) of PI films using an Abbe's 4T refractometer on the basis of the relation: $\epsilon = 1.1 \times n_{\text{av}}^2$ (at 1 kHz). The directly measured ϵ values will be also reported. Transparency of PI films in the uv-vis region was evaluated from the transmission spectra of a fixed thickness of PI films.

Results and Discussion

1. CHDA-based Polyimides

The present author has so far been studied the structural factors influencing CTE, which is closely related to the degree of in-plane orientation of PI chains.[1] Considerably low CTE values obtained in rod-like PIs such as PMDA-PDA and PMDA-TFDB and semirigid PIs such as *s*-BPDA-PDA are attributed to the spontaneous chain orientation phenomenon during thermal imidization process. For such spontaneous orientation, the PI chain linearity is a primary factor. On the other hand, it is known that one of the most effective approaches to lower the ϵ values of PI films is to introduce fluoro substituents (-

F, $-\text{CF}_3$) on the chains.[2] The use of aliphatic monomers also leads to a decreased ϵ .[3] Microporous PIs are also known as a unique approach.[4]

Another important thing to note is polyimide purity. When PI films are applied in microelectronic devices, extremely high purity is also demanded. Thus, the use of some additives (salts like LiCl, silane coupling reagents as an adhesion promoter etc.) should be limited for this purpose.

The candidates with the target properties are semi-aromatic PIs prepared by combination of aromatic dianhydrides and alicyclic diamines. Here, alicyclic diamines should have stiff/linear structures similar to p-phenylenediamine (PDA) for lowering CTE. PI systems focused first in this work are s-BPDA-CHDA and PMDA-CHDA with linear chain structures (**Fig.1**). However, one encounters a serious obstacle in the polymerization process of these PAAs. In general, the reaction systems including aliphatic diamines undergo great difficulty for obtaining high molecular weight PAA owing to the COOH/NH₂ salt formation due to much stronger basicity of aliphatic diamines than aromatic diamines. Aliphatic diamines with more stiff structures tend to result in more "tough" salt formation (gelation) on the way to PAA polymerization.

The present author successfully prepared a high molecular weight PAA of s-BPDA-CHDA without additives such as LiCl under a selected reaction condition. **Table 1** lists several data of this PI system. The obtained PI films were sufficiently flexible for practical use and exhibited much higher transparency in the ultraviolet region, a much lower ϵ , and a slightly higher CTE than the corresponding wholly aromatic PI, s-BPDA-PDA. Substituting the PDA unit for the CHDA unit caused no significant T_g decrease. Only one drawback is lower thermal stability. The weight loss in the TGA curve of this PI starts around 470°C in N₂. However, this is not important for the present purpose. This PI has sufficiently high solder resistance (T_g > 350°C).

Other CHDA-derived semi-aromatic PIs from BTDA, ODPDA, and 6FDA were also successfully prepared. However, these are rejected for the target materials in the view point of low CTE.

On the other hand, the author first failed to polymerize PMDA-CHDA for too tough gelation (salt formation). The addition of LiCl allowed the polymerization but provided a very brittle PI film unsuitable for practical use.

2. CBDA-based Polyimides

As another promising candidate for the target materials, a fluorinated semi-aromatic PI system, CBDA-TFDB can be listed up (**Fig.1**). Fluorinated diamines are in general less reactive. But, in this system, high molecular weight PAA could be readily obtained without gelation (salt formation). Thermal imidization on a glass substrate gave flexible PI

films with considerable high transparency, a high T_g (= 360°C), and a considerably low ϵ , a low CTE as listed in Table 1. Thus, CBDA–TFDB defeated a fluorinated PI, 6FDA–TFDB, (ϵ = 2.8, CTE = 48 ppm/K, T_g = 335°C) reported previously in the literature[2], although the present data do not reach to our temporal goal (ϵ = 2.5, CTE = 10 ppm/K) yet. In this presentation, other properties will be also reported.

On the other hand, CBDA–PDA, which is expected to show a lower CTE from its chain structure, gave very brittle PI films by thermal imidization on a substrate, in spite of a high molecular weight of the precursor. In general, chemical imidization usually causes lower chain orientation than thermal cure.[5] Even the chemically imidized film, however, showed a low CTE (25 ppm/K).

The effects of cure conditions, and film thickness, solvents on the film properties (ϵ , CTE, T_g, elongation at break, weight loss temperature, water uptake etc.) will be also discussed for all the PI systems shown in this work.

Polyimides	PAA η_{red} (dL/g) ^a	ϵ ^b	CTE (ppm/K) ^c	T _g (°C) ^d
s-BPDA/CHDA	2.0	3.0	23	345
CBDA/PDA	2.6	-----	25	440
CBDA/TFDB	3.1	2.66	22	360

(a) at 0.5 wt% in DMAc at 30°C

(b) estimated on the basis of average refractive index

(c) averaged within 100–200°C with a load of 0.5g/1mm-thick PI film

(d) by DMTA

References

- [1] M. Hasegawa et al., *Macromolecules*, **29**, 7897 (1996).
- [2] T. Matsuura et al., *Macromolecules*, **24**, 5001 (1991).
- [3] T. Matsumoto, et al., *Macromolecules*, **30**, 993 (1997).
- [4] J. L. Hedrick, *Adv. Polym. Sci.*, **141**, 1 (1999).
- [5] M. Hasegawa et al., *Macromolecules*, **30**, 5745 (1997).