

Properties of Polyimides Derived from Biphenyltetracarboxylic Dianhydrides and Phenylenediamines

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Abstract

This study describes some properties of polyimides (PIs) derived from two kinds of biphenyltetracarboxylic dianhydrides and two kinds of phenylenediamines. 3,3',3,4'-Biphenyltetracarboxylic dianhydride (*s*-BPDA) and 2,3',3,4'-biphenyltetracarboxylic dianhydride (*a*-BPDA) were used as acid components, and *p*-phenylenediamine (PPD) and *m*-phenylenediamine (MPD) were used as diamine components. The *s*-BPDA/PPD polyimide film showed the highest tensile modulus and the lowest coefficient of thermal linear expansion (CTE). The *a*-BPDA/PPD polyimide film showed a considerably high T_g and the lowest temperature dependence on E' below T_g in spite of its bend chain structure. The colors of polyimide films became deeper in order of *a*-BPDA/PPD, *s*-BPDA/MPD, *a*-BPDA/MPD, and *s*-BPDA/PPD, irrespective of the acidity and basicity of the corresponding monomers. The tensile moduli of polyimide films became lower in the order of *s*-BPDA/PPD, *s*-BPDA/MPD, *a*-BPDA/MPD, and *a*-BPDA/PPD. These properties of the PIs were interrelated for the first and higher order molecular structures.

Introduction

Since the polyimides indicate the excellent thermal, mechanical, and chemical properties, those have been utilized in the various kinds of field such as aerospace, semiconductor, and electronic devices. UBE Industries, Ltd. has developed a new process to synthesis BPDA¹ on an industrial scale. Applying BPDA on the acid components, PIs of unique properties are obtained, and the physical properties changes widely according to diamine components. UPILEX-S is polyimide film derived from BPDA and *p*-phenylenediamine, and has excellent heat resistance, high modulus, dimensional stability, and low coefficient of thermal linear expansion. Those properties are attributed to its rod-like structure of the molecule. On the other hand, BPDA has some isomers such as *s*-BPDA: 3,3',4,4'-biphenyltetracarboxylic dianhydride and *a*-BPDA: 2,3',3,4'-biphenyltetracarboxylic dianhydride, and phenylenediamine has also three isomers, that is, *p*-, *m*-, and *o*-phenylenediamines. A few examinations for the *a*-BPDA based-PIs have been reported.^{2,3} In this paper, we report the some properties of the PIs derived from two kinds of acid components (*s*- and *a*-BPDA) and two kinds of diamines (*p*- and *m*-phenylenediamines) in terms of the first and higher order structures.

Experimental

The *s*-BPDA/PPD films usually are manufactured in a two-step method. The first step is a polycondensation reaction between *s*-BPDA and PPD in polar solvents. This polyamic acid solution is a polyimides precursor, is then fabricated a film by solvent casting and removal of the solvent. In the second step, the resulting self-standing polyamic acid film is converted thermally to the polyimide by the removal of water at high temperatures. UBE has manufactured this type of films on an industrial scale. Since the self-standing polyamic acid films of the other composition (*s*-BPDA/MPD, *a*-BPDA/PPD, and *a*-BPDA/MPD) were too brittle, the conversion to polyimides of these films was achieved on a glass substrate under the similar cure condition for *s*-BPDA/PPD.

Results and Discussion

The mechanical properties and the coefficients of thermal linear expansion (CTEs) are listed in the Table 1. The *s*-BPDA/PPD polyimide film has the highest tensile modulus due to the rod-like backbone and the in-plane orientation. The CTEs for *s*-BPDA/PPD are generally in the range of 5~20 ppm/°C depending on the film thickness and the cure condition. Since the UPILEX-S film is usually used as the metal laminated form such as copper foil, the CTE matching is very important. The CTE for the copper foil is around 17ppm/°C, therefore, UPILEX-S is rather suitable as the insulator for the copper foil laminator such as FPC and TAB.

Table 1 Properties of PIs (at 25°C)

		<i>s</i> -BPDA/PPD	<i>s</i> -BPDA/MPD	<i>a</i> -BPDA/PPD	<i>a</i> -BPDA/MPD
Tensile Modulus	kgf/mm ²	900	370	280	310
Stress at 5% Elongation	kgf/mm ²	26	12.5	8.5	11
Elongation	%	35	25	14	20
Tensile Strength	kgf/mm ²	40	14	9.5	10.5
CTE*	ppm/°C	12	36	48	42

*Temperature Range = 50 ~ 200 °C.

On the other hand, the other PIs have rather low tensile moduli and high CTE values. The tensile moduli for *s*-BPDA/MPD, *a*-BPDA/MPD, and *a*-BPDA/PPD decrease in that order. The CTEs for these PIs become higher in that order. These are caused by the bend chain structure and the difficulty of the in-plane molecular orientation.

The chain structures for all the PIs studied in this paper, which are calculated by MM method, are shown in Figure 1. This simulations are for the molecules consisting by six units. The end-to-end distances decrease in the order of *s*-BPDA/PPD, *s*-BPDA/MPD, *a*-BPDA/MPD, and *a*-BPDA/PPD. The values of tensile modulus and CTE reflect the end-to-end distance or the aspect ratio of the polymer chain. Though the *a*-BPDA/MPD polyimide has two bend linkage per a unit, the magnitude of the orientation differs from the intuition.

The dynamic tensile moduli, E' , E'' , and $\tan \delta$ are plotted as a function of temperature in Figures 2 and 3 for the *s*-BPDA/PPD and *a*-BPDA/PPD, respectively. Those for *s*-BPDA/MPD and

a-BPDA/MPD resemble rather to Figure 3 than Figure 2.

The *s*-BPDA/PPD polyimide does not show a distinct T_g, and this is attributed to both the polyimide backbone stiffness and the presence of crystallinity. The value of E' indicates of the order of 10¹⁰ dynes/cm² even at above 400°C. The other PIs have narrow glass transition at 350, 355, and 430°Cs for *s*-BPDA/MPD, *a*-BPDA/MPD, and *a*-BPDA/PPD, respectively. The two or three order decrease of the tensile modulus through the glass transition for these PIs is due to the low or lack of crystallinity. Since the PIs derived from *a*-BPDA have asymmetric backbone, the crystallinity is extremely restricted. Therefore, most of them have no distinct crystallinity.³

The profile of E' for *a*-BPDA/PPD shows very low dependence on temperature, and the β and γ relaxations are not clear. These relaxations are explained by the terms of rotational and mutual motions of polymer segments. The complicated backbone morphology for the *a*-BPDA-based PIs causes the restriction of molecular motion. This may be due to the extremely high T_g for *a*-BPDA/PPD. The T_g for *a*-BPDA-based PIs consisting *p*-linked aromatic diamines is usually higher than that for the corresponding *s*-BPDA-based PIs.³

The UV-Vis absorption spectra for all the PIs (thickness: 20 μm) are shown in Figure 4. The color intensities of polyimide films are generally explained by the electronic properties of their source monomers.⁴ The colors become deeper with increasing the electron-accepting properties of the dianhydrides and increasing the electron-donating ones of the diamines. The electron-accepting property of *s*-BPDA is higher than that of *a*-BPDA, and the electron-donating one of PPD is higher than that of MPD.⁵ Standing the upper view point, the color of *a*-BPDA/PPD should become deeper than that of *a*-BPDA/MPD. The wavelenghtes of the absorption edge for *s*-BPDA/PPD, *s*-BPDA/MPD, *a*-BPDA/PPD, and *a*-BPDA/MPD are 425, 400, 385, and 380 nms, respectively. These can be explained by the electronical properties of the monomers. On the other hand, the color intensity of *a*-BPDA/MPD in the visible region is rather high as compared with the others. This polyimide may be in the suitable conformation for the intermolecular charge-transfer formation.

Conclusions

The physical and mechanical properties for the four kinds of isomeric polyimides having rigid backbones can be characterised by the molecular structures. The rod-like PI such as *s*-BPDA/PPD shows high tensile modulus and low CTE. The PI having complicated molecular structure such as *a*-BPDA/PPD shows rather low tensile modulus, high CTE, and high T_g. These can be explained by the terms of in-plane backbone orientation and restriction of molecular motion. The *s*-BPDA/PPD polyimide films are now widely utilized in the various fields as UPILEX-S series.

References

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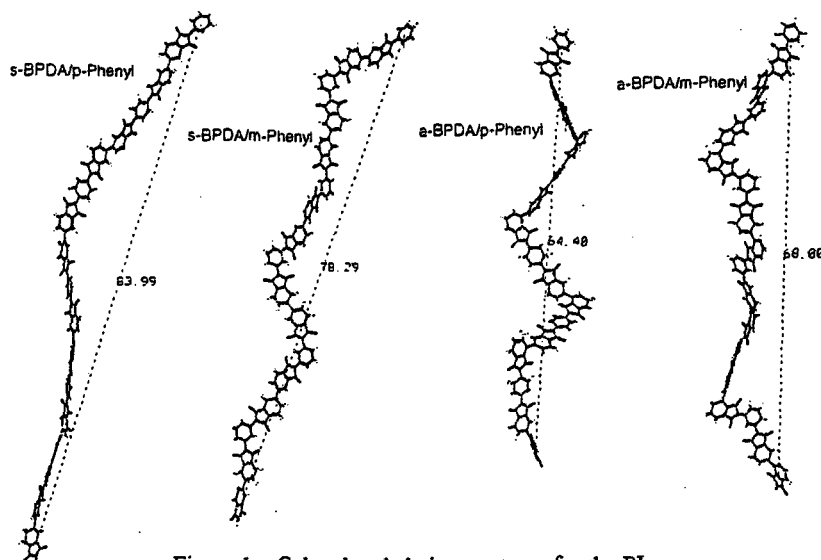


Figure 1 Calculated chain structures for the PIs.

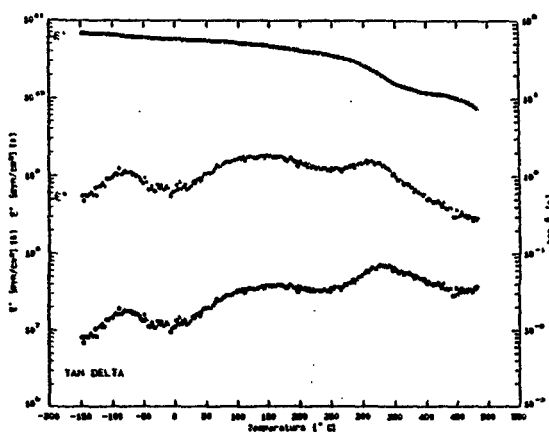


Figure 2 Viscoelastic analyses of *s*-BPDA/PPD

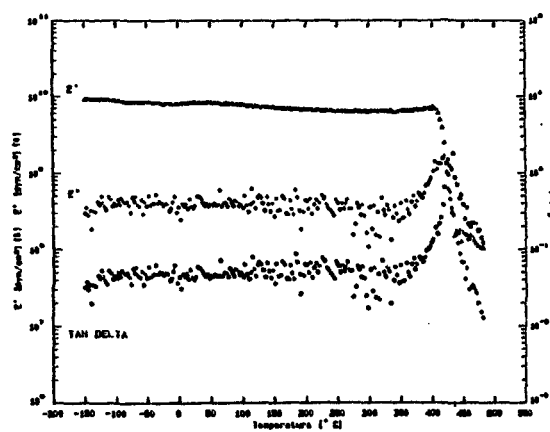


Figure 3 Viscoelastic analyses of *a*-BPDA/PPD

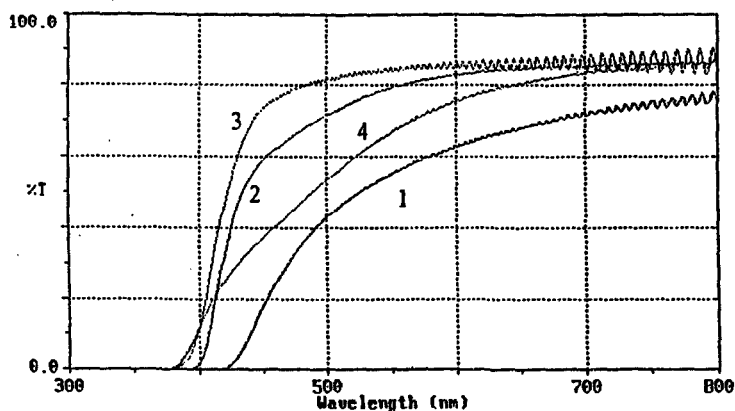


Figure 4 UV-Vis absorption spectra.

1:*s*-BPDA/PPD, 2:*s*-BPDA/MPD, 3:*a*-BPDA/PPD, and 4:*a*-BPDA/MPD.