Polyimides with a Large Optical Anisotropy

U. Goeschel

Tokyo University of Agriculture and Technology, Department of Material Systems-Engineering, 2-24-16 Nakamachi, Koganei Tokyo 184

INTRODUCTION

Polyimides with their outstanding mechanical and electrical properties, thermal and chemical stability, have become increasingly important as high performance material as well as interlayer dielectrics or photoresists in microelectronic devices. Controlable chain orientation and molecular order along with the anisotropy in the dielectric constant and the coefficient of thermal expansion (CTE) enable novel applications in electronic packaging structures. [1]

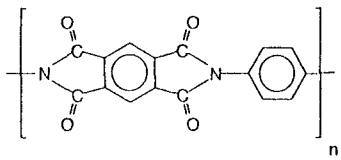
Thin polyimide films prepared by thermal imidization after film casting can differ strongly in their data for the optical anisotropy. Using a polarized laser light at 632.8 nm, we determined a difference between the in-plane and out-of-plane refractive index (Δn) of 0.017 for a poly(phenylquinoxaline) (PPQ) and 0.242 for poly(p-phenylene biphenyltetracarboximide) (BPDA-PDA). To gain new insights into the structure-property relationships of polyimides with an extraordinarily large optical anisotropy, two chemically different polyimides prepared by thermal imidization of two kinds of precursors were characterized with respect to their optical, thermo-mechanical and structural properties [2] and discussed in relation to other aromatic polyimides.

EXPERIMENTAL

Materials

Poly(p-phenylene pyromellitimide) (PMDA-PDA) and poly(p-phenylene biphenyltetracarboximide) (BPDA-PDA) (*Figure 1*) were prepared by thermal imidization of the respective poly(amic acid) and poly(amic ethyl ester) precursors [2]. The two precursors should yield the same chemical polyimide structure. N-methylpyrrolidone (NMP) was used as solvent.

PMDA - PDA



BPDA - PDA

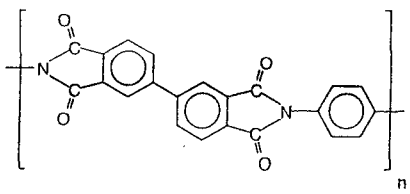


Figure 1: Polyimide structures.

Thin films were prepared by film casting of the respective polyimide precursor solutions onto suiteable substrates. The drying was performed immediately after coating by slow heating at 1 °C/min from room temperature to 125 °C and holding this temperature constant for 60 min. The imidization took place during heating from 125 to 400 °C at 5 °C/min and thermal annealing at 400 °C for 60 min.

Measurements

The attenuated total reflection (ATR) spectroscopy was used to determine the in-plane and out-of-plane refractive indices by means of the reflected intensity as a function of the angle of incidence for TE and TM polarization, respectively at a wavelength of 632.8 nm. The polymer film thickness was

choosen from 860 to 2600 nm (*Figure 2*).

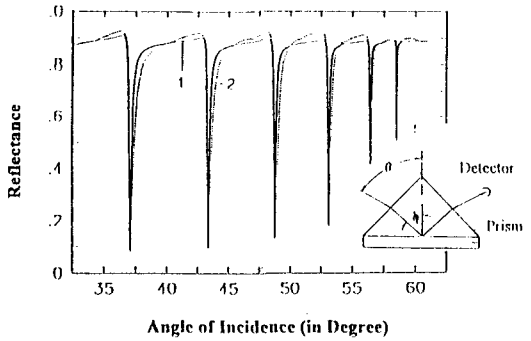


Figure 2: ATR spectroscopy of the waveguide modes. The theoretical curve (1) is fitted to the measured curve (2) for the BPDA-PDA from poly(amic ethyl ester) precursor.

The thermal mechanical analysis (TMA) experiments were performed in the temperature range from 25 to 400 °C under helium atmosphere using a heating and cooling rate of 5 °C/min. From the change of the specimen length as function of the temperature under constant low force, the coefficients of thermal expansion (CTEs) were determined within the temperature range from 150 to 300 °C.

Using a Polymer Laborties DMTA in tensile mode, the dynamic mechanical thermal analysis (DMTA) provided the storage (E') and loss modulus (E") in the temperature range from -50 to 400 °C at a frequency of 10 Hz. The sample thicknesses ranged from 6 to 46 μm. The heating rate was 5 °C/min, consistent with the TMA experiments. The moduli were taken from the second run, following 400 °C.

Wide angle X-ray diffraction (WAXD) patterns were obtained in reflection and transmission mode. A Siemens Diffractometer Model D5000 providing a X-ray beam of 1.5418 Å (Angstrom) combined with a Kevex detector was used. The sample thicknesses were chosen in the range from 2.5 to 64 μm.

RESULTS AND DISCUSSION

ATR Spectroscopy studies. The results are shown in *Table 1* by using the in-plane (n_{TE}) and out-of-plane (n_{TM}) refractive indices, the birefringence, $\Delta n = n_{TE} - n_{TM}$, and the average refractive indices, $\bar{n} = (2n_{TE} + n_{TM})/3$. Here, n_{TE} and n_{TM} denotes the refractive indices perpendicular and parallel to the film plane, respectively. The expression for the average refractive index is valid for the case of an isotropy in the film plane. According to ATR optical waveguide experiments with polarized laser light at 632.8 nm, PMDA-PDA and BPDA- PDA polyimides exhibit an

Table 1: Refractive indices of several polyimides

Precursor Sample	Refractive Index Data		Birefringence	Average Refractive Index
	n_{TE}	n_{TM}	Δn	$\bar{n}$
PMDA-PDA (acid)	1.810	1.612	0.198	1.744
PMDA-PDA (ester)	1.816	1.600	0.216	1.744
PMDA-ODA (acid)[3]	1.721	1.643	0.078	1.695
BPDA-PDA (acid)	1.856	1.614	0.242	1.775
BPDA-PDA (ester)	1.845	1.615	0.230	1.768
PPQ*	1.774	1.757	0.017	1.768

* Solvent: m-cresol

unusually large anisotropy between the in-plane and out-of-plane refractive indices, with the larger values observed for the semi-rigid BPDA-PDA (*Table 1*). The birefringences (Δn) ranged from 0.198 to 0.216 for PMDA-PDA and from 0.230 to 0.242 for BPDA-PDA. Under the same conditions for imidization and ATR waveguide measurement for all samples in *Table 1*, the optical anisotropy (Δn) of PMDA-PDA as well as BPDA-PDA is larger than for the familar PMDA-ODA structure with $\Delta n = 0.078$ [3] and much larger than for the nearly isotropic and aromatic PPQ with $\Delta n = 0.017$. The birefringence of PMDA-PDA and BPDA-PDA is also larger than those of most of the fluorinated polyimides with $0.004 \leq \Delta n \leq 1.608$ [4]. The film thicknesses in our experiments ranged from 860 to 2600 nm and revealed no influence on the refractive index data.

Thermal mechanical analysis (TMA). The dimension changes in the sample length as function of temperature showed the expected high temperature resistence and very low coefficients of the thermal expansion (CTEs) in the case of the PMDA-PDA and BPDA-PDA polyimides. Independent from the precursor used, both polyimides exhibited a linear increase in the sample length from 60 up to 350 °C. Cooling down to 60 °C caused a decrease in the length along the previous trace without significant hysteresis effects. A second heating from 60 to 350 °C showed a reversible thermal behavior [2]. At temperatures in excess of 350 °C the rigid PMDA-PDA revealed a shrinkage whereas the semi-rigid BPDA-PDA showed a softening at temperatures obove 325 °C. The CTEs determined over the temperature range 100 to 300 °C was found to be 6.5 and 8.2 ppm/°C for PMDA-PDA derived from poly(amic acid) and poly(amic ethyl ester) precursors, respectively [2]. Contrary to that, the CTEs of BPDA-PDA revealed a strong influence of the precursors. As shown in *Figure 3*, the CTE of the poly(amic acid)-derived BPDA-PDA was only 4.3 ppm/°C compared with 18 ppm/°C for the poly(amic ethyl ester)-derived BPDA-PDA [2].

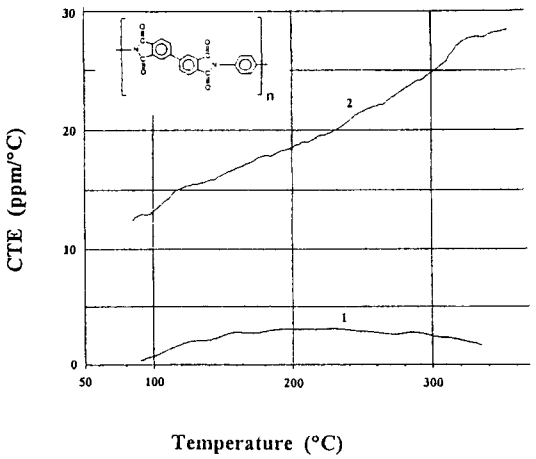


Figure 3: Coefficients of thermal expansion (CTEs) for BPDA-PDA polyimides prepared from the (1) poly(amic acid) and (2) poly(amic ethyl ester) precursors.

Dynamic mechanical thermal analysis (DMTA). With respect to DMTA measurements in the temperature range from 25 to 400 °C only a small change of the storage modulus (E') which corresponds to the material stiffness was found for the rigid PMDA-PDA. Rostojstaczer *et al.* [5] discussed for PMDA-PDA from poly(amic ethyl ester) only a gradual decrease in the storage modulus up to 500 °C without any transitions due to changes in the molecular mobility. As shown in *Figure 4*, the semi-rigid BPDA-PDA exhibits a softening in the temperature range from 325 to 400 °C. The decrease in the E' modulus is somewhat larger for BPDA-PDA polyimide derived from the poly(amic ethyl ester) precursor than for the poly(amic acid)-derived counterpart.

Wide angle X-ray diffraction (WAXD) studies. The WAXD patterns obtained in reflection and transmission mode revealed a large anisotropy in the supermolecular struc-

ture of PMDA-PDA as well as BPDA-PDA. Parallel to the film surface the structure was isotropic.

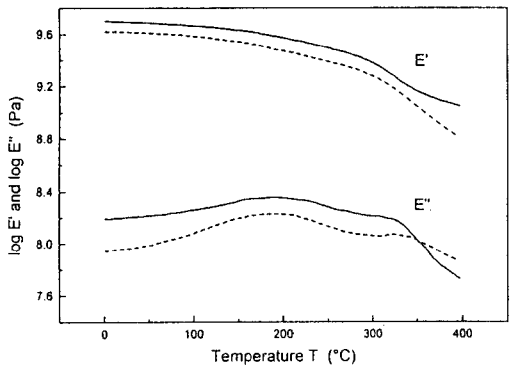


Figure 4: Temperature dependence of the dynamic storage (E') and loss modulus (E") at 10 Hz for BPDA-PDA polyimide films from (—) poly(amic acid) and (- -) poly(amic ethyl ester) precursors.

The molecular chains are highly aligned in the film plane with well-defined monomeric repeat layers, analogous to smectic states [2]. Taking the peak designations from ref. [6], *Figure 5* represents the (004), (110), (00,10), (00,14), and (00,16) reflexes for BPDA-PDA.

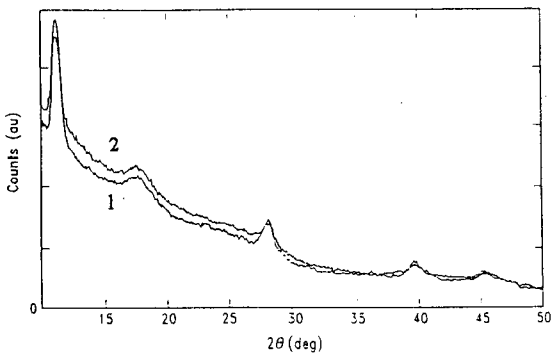


Figure 5: WAXD transmission patterns of BPDA-PDA polyimides prepared from the (1) poly(amic ethyl ester) and (2) poly(amic acid) precursors. Thickness of the free-standing film: 16 μm.

The lateral order of PMDA-PDA and BPDA-PDA polyimides was only low. A better lateral packing of the molecular chains was found for the polyimides prepared from poly(amic ethyl ester) precursors, as seen for BPDA-PDA in *Figure 6*.

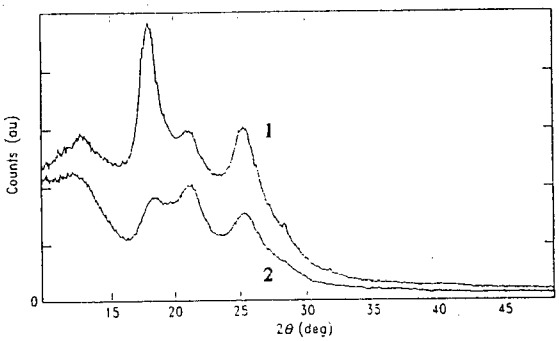


Figure 6: WAXD reflection patterns of BPDA-PDA polyimides prepared from the (1) poly(amic ethyl ester) and (2) poly(amic acid) precursors. Thickness of the free-standing film: 5.5 μm.

REFERENCES

1. Tummala, R.R. and Rymaszewski, E.J. *Microelectronics Packaging Handbook*, New York, Van Nostrand-Reihold, 1989
2. Goeschel, U., Lee, H., Yoon, D.Y., Siemens, R.L., Smith, B.A., and Volksen, W. *Colloid Polym. Sci.* 1994, **272**, (11), 1388
3. Russel, T.P., Gugger, H., and Swalen, J.D. *J. Polym. Sci., Polym. Phys. Ed.* 1983, **21**, 1745
4. Ando, S., Matsuura, T., and Sasaki, S. *ACS Symposium Series* 1994, **537**, 304
5. Rojstaczer, S., Ree, M., Yoon, D.Y., and Volksen, W. *J.Polym. Sci., Polym. Phys. Ed.* 1992, **30**, 133
6. Yoon, D.Y., Depero, L.E., Parrish, W., and Ree, M. *Mat. Res. Soc. Symp. Proc.* 1991, **227**, 387