Colloid & Polymer Science Colloid Polym Sci 272:1388–1395 (1994)

Effects of chemical structure and precursor on optical properties, thermo-mechanical properties, and molecular orientation and order of thin films of stiff aromatic polyimides*)

U. Goeschel, H. Lee, D. Y. Yoon, R. L. Siemens, B. A. Smith, and W. Volksen

IBM Research Division, Almaden Research Centre, San Jose, California

*) *Dedicated to Prof E. W. Fischer on the occasion of his 65th birthday*

Abstract: Thin films of rigid poly(*p*-phenylene pyromellitimide) (PMDA-PDA) and semi-rigid poly(*p*-phenylene biphenyltetracarboximide) (BPDA-PDA), prepared by thermal imidization of the respective poly(amic acid) and poly(amic ethyl ester) precursors, were characterized with respect to their optical, thermo-mechanical and structural properties. Both polyimides exhibit an unusually large anisotropy between the in-plane and out-of-plane refractive indices, with Δn ranging from 0.198 to 0.216 for PMDA-PDA and from 0.230 to 0.242 for BPDA-PDA, nearly independent of the nature of the initial polyimide precursor, film thickness, and film preparation method. PMDA-PDA films exhibit low coefficients of thermal expansion (CTE's) of 6.5 and 8.2 ppm/°C for the acid-derived and the ester-derived polyimides, respectively. In comparison, the BPDA-PDA films show CTE values of 4.3 and 18.0 for the acid-derived and ester-derived samples, respectively, despite the small differences in their optical anisotropies. Wide-angle x-ray diffraction patterns obtained in reflection and transmission for the various samples reveal a strong in-plane chain orientation for both PMDA-PDA and BPDA-PDA polyimides, with somewhat better intermolecular packing order for the ester-derived polyimide films. These effects of chemical structure and precursor on properties and structures of the polyimide films are discussed in light of recent theoretical considerations of semiflexible polymers.

Key words: Polyimides – optical properties – thermo-mechanical properties – chain orientation – conformational order – poly(amic acid) – poly(amic alkyl ester).

Introduction

Semi-rigid and rigid polyimides have been of great interest for microelectronic applications because of their outstanding thermal, electrical, and mechanical properties along with relatively low coefficients of thermal expansion (CTE's) [1–3]. The polyimides poly(*p*-phenylene pyromellitimide) (PMDA-PDA) and poly(*p*-phenylene biphenyltetracarboximide) (BPDA-PDA) represent the two most prominent examples. Traditionally, these polyimides have been prepared by the thermal cyclization of poly(amic acid), based in part on the readily available starting monomers and ease of preparation of the corresponding poly(amic acid). More recently, use of poly(amic alkyl esters) for the preparation of thin polymide structures has been reported [4]. Such polyimide precursors are similarly cyclized to the final polyimide by thermal means, although imidization temperatures tend to be somewhat higher than required for corresponding poly(amic acids) [5]. In spite of the more elaborate synthetic procedure required to produce poly(amic alkyl esters), they exhibit greater solution stability and generally yield more processable formulations. Irrespective

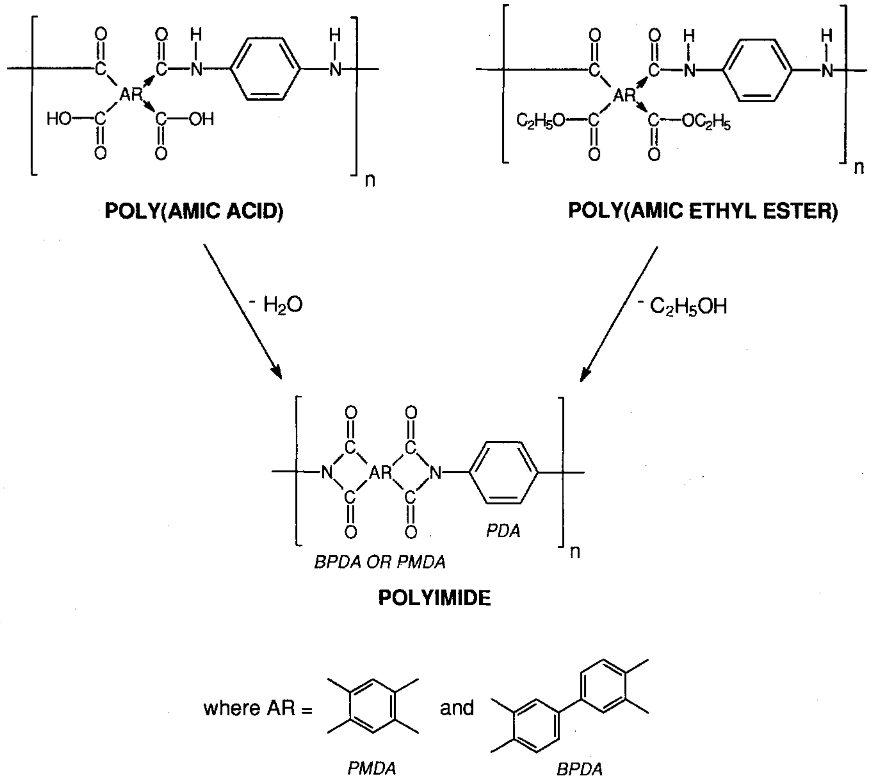

Fig. 1. Chemical structure of PMDA-PDA polyimide, prepared from the precursors poly(amic acid) and poly(amic ethyl ester) as well as the BPDA-PDA polyimide, prepared from the precursor poly(amic acid) and poly(amic ethyl ester)

of the starting precursor, identical chemical structures of the final polyimide are obtained.

Although various properties associated with the polyimides based on BPDA-PDA and PMDA-PDA as derived from both poly(amic acid) and poly(amic alkly ester) precursors (see Fig. 1) have appeared in the literature, the systematic study of BPDA-PDA and PMDA-PDA polyimides as derived from both types of precursor with respect to optical and thermo-mechanical properties does not exist. Therefore, in light of the relative importance of these two polyimides concerning high-tech applications, we present the comparision of structure-property relationships of these two polyimides as prepared from the corresponding poly(amic acid) and poly(amic ethyl ester) with identical thermal histories.

Experimental

Materials

BPDA-PDA and PMDA-PDA poly(amic acids) were prepared from freshly sublimed monomers in dry *N*-methylpyrrolidone (NMP), utilizing a stoichiometric imbalance, $r = 0.980$, with *p*-phenylene diamine (PDA) representing the monomer being used in excess. The ratio of monomers to solvent was adjusted so as to yield a final poly(amic acid) concentration of ca. 10 wt%. All polymerizations were performed in a glove box under a helium atmosphere. Under such conditions, it has been shown that well-defined poly(amic acids) with average degrees of polymerization of ca. 100 can be produced [6]. These solutions were then directly utilized for thin film preparation. The corresponding poly(amic ethyl esters) were obtained according to previously reported procedures [7, 8]. In the case of the PMDA-based poly(amic ethyl ester) system the meta-PMDA diester was employed to facilitate better solubility. For the BPDA-based poly(amic ethyl ester) the isomeric mixture as obtained from the initial esterification reaction was employed. The ester precursor solutions for thin film preparation were prepared by freshly dissolving the solid precursor in NMP to yield polymer concentrations ranging from 10–15 wt%.

Thin film preparation

Polyimide thin films were prepared by spin-coating or doctor-blading the respective polyimide precursor solutions, which had been carefully filtered through 1 μm Millipore filters, onto suitable substrates, followed by drying and finally thermal imidization. The thermal history of all samples was as follows: immediately following the coating step, samples were heated at 1 °C/min from room temperature to 125 °C and held at this temperature for 60 min; the sample was then further heated at 5 °C/min from 125° to 400 °C, followed by thermal annealing at 400 °C for 60 min. Free-standing films could then be obtained by scoring the edges of the deposited film and immersing the substrate in water. The film thickness of free-standing films was measured with a micrometer, whereas coatings were measured on an Alpha Step 200 from Tencor Instruments.

Attenuated total reflectance (ATR) spectroscopy

Thin films, prepared on gold-coated optical glass substrates having a polymer film thickness from 0.86 to 2.60 μm, were investigated at room temperature by optical waveguide spectroscopy. In this method [9], a polarized He-Ne laser (632.8 nm wavelength) and a high refractive index prism ($n = 1.8795$), coupled with the coated optical glass substrate, were used. The reflected intensity as function of the angle of incidence was measured for TM and TE polarization, respectively. By fitting the theoretical curves on the basis of Fresnel's formulae to the measured waveguide spectra [10] two refractive index values (in-plane, $n_{\parallel}$, and out-of-plane, $n_{\perp}$) of the polymer films were obtained.

Thermal mechanical analysis (TMA)

The coefficients of thermal expansion (CTE's) were obtained by measuring the change in specimen length as a function of temperature while applying a constant and low force. The experiments were carried out in the temperature range from 25° to 400 °C under helium atmosphere, using a heating and cooling rate of 5 °C/min. The sample thicknesses varied from 0.8 to 6.0 μm. For the resulting cross-sections from 3.4 to 16.5 mm^2 forces from 0.015 N to 0.020 N were chosen. These forces were within the linear range of the stress-strain curve at room temperature. An initial sample length of 8.9 mm was used. The CTE values were taken from the temperature range 100° to 300 °C, following a slow cooling from 400 °C. To minimize statistical effects, at least six samples for each thickness and used precursor were investigated.

Dynamic mechanical thermal analysis (DMTA)

The experiments were performed on a Polymer Laboratories DMTA in the tensile mode at a frequency of 10 Hz. Sample geometries were 20 mm in length, 6 mm in width, and thicknesses ranging from 6 to 46 μm. The heating rate was 5 °C/min, consistent with the TMA experiments. The modulus values were taken from the second heating run, following cooling from 400 °C.

Wide angle X-ray diffraction (WAXD)

The WAXD patterns were obtained in transmission mode (i.e., reflections from lattice planes normal to the film surface) and in reflection mode (i.e., reflections from lattice planes parallel to the film surface). For both experiments a Siemens Diffractometer Model D5000, combined with a Kevex detector, was used. The patterns were recorded using a step scanning with 0.05 degree steps and 200 s count time per step for the transmission and 4 s for the reflection, respectively. The source, 50 kV and 300 mA, provided an x-ray beam of 1.54 Å wavelength. In the case of transmission experiments a primary slit of 0.2 mm, an anti-scatter slit of 2 mm, and a secondary slit of 0.6 mm were used. For reflection the primary slit was changed to 2 mm. The sample thicknesses were chosen in the range from 2.5 to 64 μm. Reflection experiments were performed on spin-coated films onto (100) silicon wafers as well as on free-standing films. In the case of the transmission mode, free-standing films were used.

Results and Discussion

ATR spectroscopy

The polyimides derived from the two sets of precursors display an extraordinarily large anisotropy in the refractive indices as expected based

Table 1. Optical and thermo-mechanical data of PMDA-PDA and BPDA-PDA polyimides

Precursor Samples	Refractive Index Data[a]) $n_{\parallel}$	$n_{\perp}$	Δn	$\bar{n}$	Thermo-mechanical data CTE (ppm/°C)[b])
PMDA-PDA (acid)	1.810	1.612	0.198	1.744	6.5
PMDA-PDA (ester)	1.816	1.600	0.216	1.744	8.2
BPDA-PDA (acid)	1.856	1.614	0.242	1.775	4.3
BPDA-PDA (ester)	1.845	1.615	0.230	1.768	18.0

[a]) Refractive indices were determined at 632.8 nm
[b]) CTE determined over the temperature range 100°C to 300 °C

on earlier reports [9, 11] utilizing the poly(amic acid) precursors. The results from the attentuated total reflectance (ATR) spectroscopy are shown in Table 1, comparing the in-plane ($n_{\parallel}$) and out-of-plane ($n_{\perp}$) refractive indices along with the differences between these values (Δn), and the average refractive index ($\bar{n} = (2n_{\parallel} + n_{\perp})/3$). Film thicknesses ranging from 0.86 to 2.6 μm were employed and no significant effect of film thickness on the values of the refractive indices was observed. Furthermore, no discernable difference was found between the spin-coated and doctor-bladed film preparations.

In all cases the in-plane refractive index is much larger than the out-of-plane refractive index. Sampling of the polyimide film at various locations over the substrate surface revealed absolutely no variation in these values. The observed Δn of about 0.20 for the PMDA-PDA polyimides and ca. 0.24 for the BPDA-PDA polyimides represents an extremely large optical anisotropy, much higher than values reported for other polymers including polyimides [12–15]. This indicates a preferred polarization axis in the plane of the polyimide film and, hence a preferred orientation of the polyimide chain in the film plane. In the case of the BPDA-PDA based polyimide our results are consistent with earlier reported values for the same polymer as derived from the poly(amic acid) [9, 11]. It is interesting to note that for a given polyimide as derived from the two different precursors, Δn differs only by 5% and 9% for the BPDA-PDA and PMDA-PDA system, respectively. Therefore, the above optical anisotropy data indicate no significant influence of the polyimide precursor on the molecular orientation in the final polyimide films as obtained by thermal imidization. Moreover, the variation of Δn of the final polyimide films as a function of the precursor employed does not show any consistent trend.

Thermo-mechanical analysis

In addition to optical anisotropy measurements, the orientation of the PMDA-PDA and BPDA-PDA chains should manifest itself in both the thermo-mechanical properties as evidenced by the coefficient of thermal expansion (CTE) and the dynamic mechanical properties as reflected by the storage modules, E', and the loss tangent, tan δ. With respect to TMA experiments, dimensional changes in sample lengths as a function of temperature were measured in the range of 60° to 400 °C. As shown in Fig. 2, both PMDA-PDA based polyimide films as prepared from the two precursors exhibit a linear increase of the sample length up to 350 °C. Cooling the specimens from 350° back down to 60 °C causes a decrease in the sample length essentially along the previous TMA trace without significant hysterisis effects. A second heating from 60° to 350 °C exhibits a reversible thermo-mechanical behavior. At temperatures in excess of 350 °C shrinkage occurs for both cases. Thus, although the overall thermo-mechanical behavior of the poly(amic acid) and poly(amic ethyl ester) derived polyimides are similar, the poly(amic ethyl ester) derived polyimide exhibits a somewhat larger CTE than the corresponding poly(amic ethyl acid) derived sample; see Fig. 2. The resulting CTE values are tabulated in Table 1.

It is apparent that the CTE values for PMDA-PDA films derived from the poly(amic acid) and

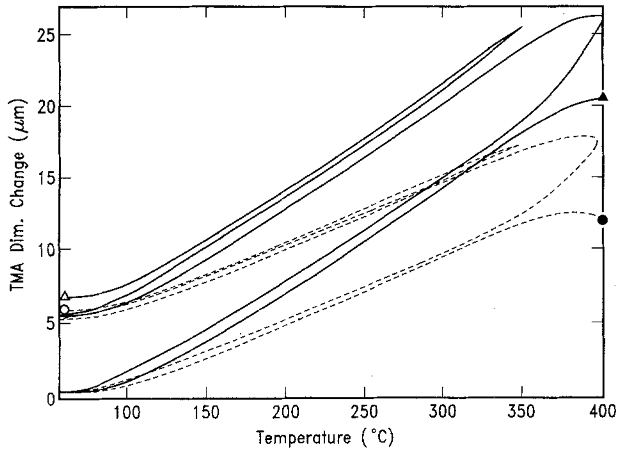

Fig. 2 Dimensional change with temperature for PMDA-PDA polyimides, prepared from the precursors poly(amic acid) (---) and poly(amic ethyl ester) (—). Temperature changes: 60 – 350 – 60 – 400 – 60– 400 °C. △ and ○ denote the starting point, while ▲ and ● indicate the final point of the ester and acid, respectively

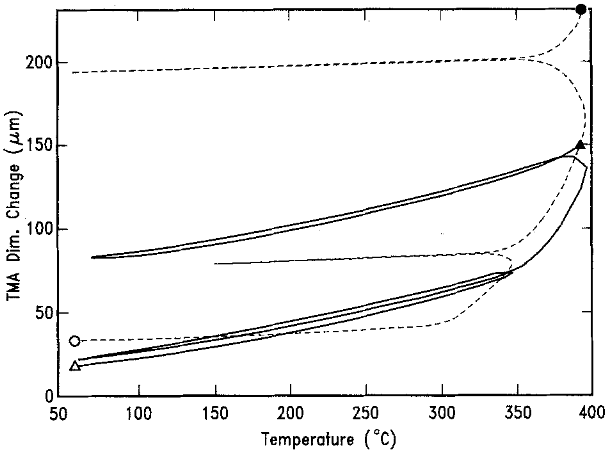

Fig. 3. Dimensional change with temperature for BPDA-PDA polyimides, prepared from the precursors poly(amic acid) (---) and poly(amic ethyl ester) (—). Temperature changes: 60 – 350 – 60 – 400– 60– 400 °C. △ and ○ denote the starting point, while ▲ and ● indicate the final point of the ester and acid, respectively

poly(amic ethyl ester) are relatively small, with the CTE of the poly (amic ethyl ester) derived polyimide being quite consistent with the values previously reported [16]. In the case of the polyimide specimens derived from the BPDA-PDA based poly(amic acid) and poly(amic ethyl ester), respectively, similar behavior as compared to the PMDA-PDA system is observed in the temperature regime of 60° to 300 °C; see Fig. 3. In case of the poly(amic acid) derived BPDA-PDA specimen one observes a relatively small CTE up to a temperature of 300 °C upon the first heat. Further heating to 350 °C causes an increase in the dimensional change of the specimen as expected for softening behavior. Cooling of the specimen and second heating produce a shift in this softening temperature to 350 °C where it remains during further cooling and heating cycles. In contrast, the poly(amic ethyl ester) derived BPDA-PDA specimen exhibits the softening behavior at 350 °C on the first heating cycle. Upon cooling and second heating this softening shifts to slightly higher temperatures where it remains during further cooling and heating cycles. The most surprising result becomes apparent upon comparison of the absolute CTE over the temperature range of 100 °C to 300 °C, as listed in Table 1. The CTE for the poly(amic acid) derived BPDA-PDA polyimide of 4.3 ppm/°C was even smaller than those of the PMDA-PDA based samples. The CTE of 18 ppm/°C for the poly(amic ethyl ester) derived polyimide was quite unexpected in view of the nearly identical optical anisotropy as compared to that of the acid-derived sample. It is important to keep in mind that all specimens had the same thermal history, i.e., 400 °C for 1 h, prior to the TMA experiments. In addition, film thicknesses ranging from 0.8 to 6.0 μm were checked without indication of any film thickness effect on the TMA properties.

Supplemental to the thermo-mechanical analysis, dynamic mechanical thermal analysis (DMTA) was also performed. At room temperature, measurements indicate storage moduli of the various polyimide specimens between 4 and 10 GPa for both PMDA-PDA and BPDA-PDA based polyimides irrespective of the precursor employed. These values are consistent with the values found by Rojstaczer et al. [16] for PMDA-PDA derived from the poly(amic ethyl ester) and by Smith and Kim [17] for BPDA-PDA derived from the poly(amic acid). The change of the storage modulus with temperature, over the temperature range 25° to 400 °C, is smaller for PMDA-PDA polyimide as compared to BPDA-PDA polyimide. This is not unusual, since the BPDA-PDA polyimide is not quite as linear as the PMDA-PDA based system. In the case of PMDA-PDA, no softening temperature is apparent at temperatures well above 400 °C. In

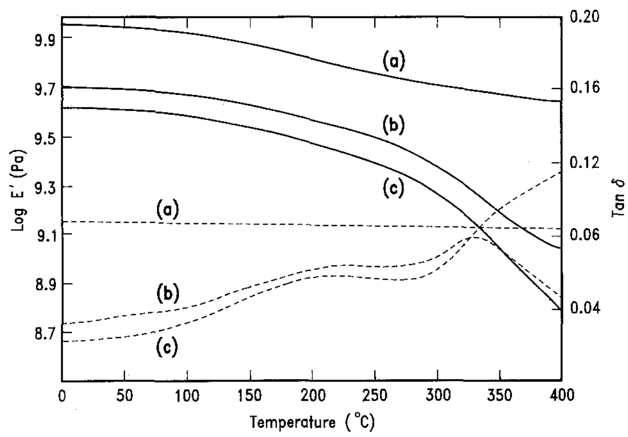

Fig. 4. Comparison of the temperature dependence of the storage modulus E', (—), and tanδ, (---) for PMDA-PDA polyimide as derived from the poly(amic ethyl ester), (a), and BPDA-PDA polyimides, prepared from the precursors poly(amic acid), (b), and poly(amic ethyl ester), (c)

contrast to PMDA-PDA based polyimides, BPDA-PDA polyimides exhibit a transition temperature in the vicinity of 350 °C consistent with the softening behavior observed in the TMA experiments; see Fig. 4.

Wide-angle X-ray diffraction studies

WAXD reflection patterns of PMDA-PDA from poly(amic acid) as well as poly(amic ethyl ester) exhibit three significant peaks at 20.9, 26.4, and 36.0 degrees, above a broad halo in the 2Θ range from 10 to 50 degrees (Fig. 5). In the case of PMDA-PDA from poly(amic ethyl ester) our WAXD patterns are consistent with ref. [16]. The reflection patterns of PMDA-PDA characterize a polymer structure with a low degree of lateral order. From the differences in the relative peak intensities in the reflection patterns (Fig. 5), a better packing of the molecular chains can be derived for PMDA-PDA from poly(amic ethyl ester) compared to the poly(amic acid) derived polyimide. The WAXD transmission pattern of PMDA-PDA exhibits several sharp peaks; see Fig. 6. According to ref. [16], these are the *00l* peaks (002 to 006). The peak positions do not change significantly with the precursors used for the imidization. The comparison between the WAXD transmission and reflection pattern show a large anisotropy in the structure of PMDA-PDA, consistent with molecular orientation along the film plane.

In Fig. 7 the WAXD reflection patterns of 5.5 μm free-standing BPDA-PDA films are seen. The pattern in the 2Θ range from 10 to 50 degrees exhibits three peaks at 18.1, 21.1, and 25.4 degrees above a broad halo, in agreement with previous results [18]. According to ref. [19] these reflection peaks are the 110, 200, and 210 peaks. In ref. [19], which utilized 25-μm-thick films, the 200 peak does not exist. From the reflection pattern in Fig. 7 we derive a better lateral packing order of the molecular chains for BPDA-PDA from the poly(amic ethyl ester) precursor than from poly(amic acid). The WAXD transmission pattern of both BPDA-PDA films, Fig. 8, shows five

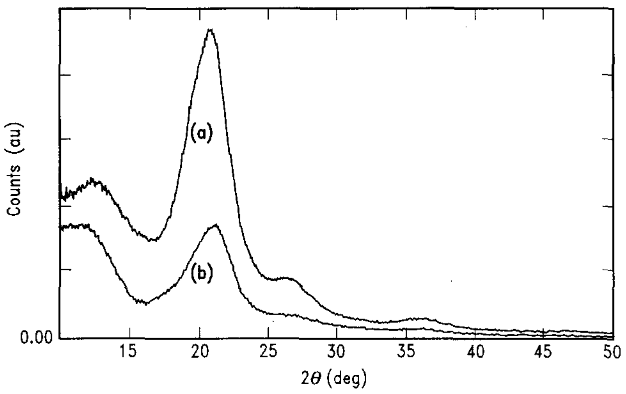

Fig. 5. WAXD refelction patterns of PMDA-PDA polyimides, prepared from the precursors (a) poly(amic ethyl ester) and (b) poly(amic acid). Film thicknesses: 5 μm, free-standing films

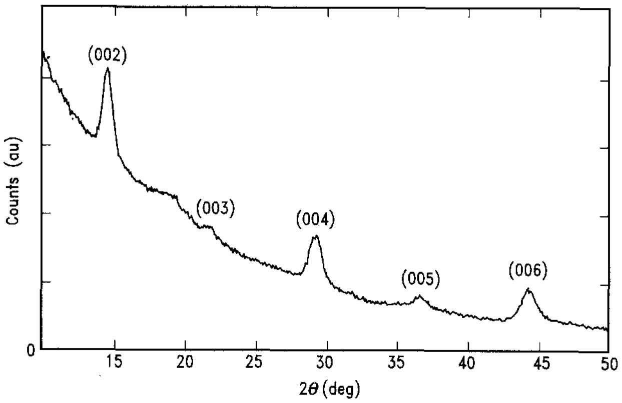

Fig. 6. WAXD transmission patterns of PMDA-PDA polyimides, prepared from the poly(amic ethyl ester) precursor. Film thicknesses: 5 μm, free-standing films. The results for acid-derived films are pratically the same.

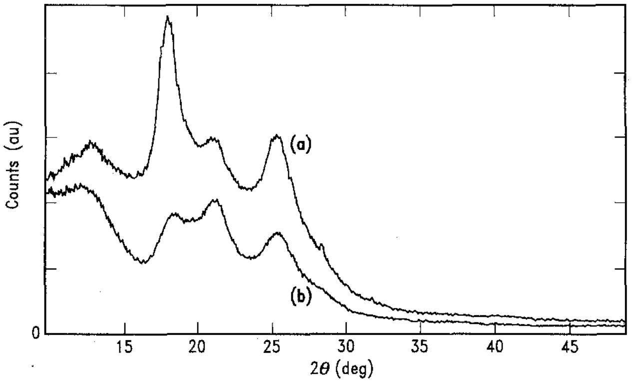

Fig. 7. WAXD refelction patterns of BPDA-PDA polyimides, prepared from the precursors (a) poly(amic ethyl ester) and (b) poly(amic acid). Film thicknesses: 5.5 μm, free-standing films

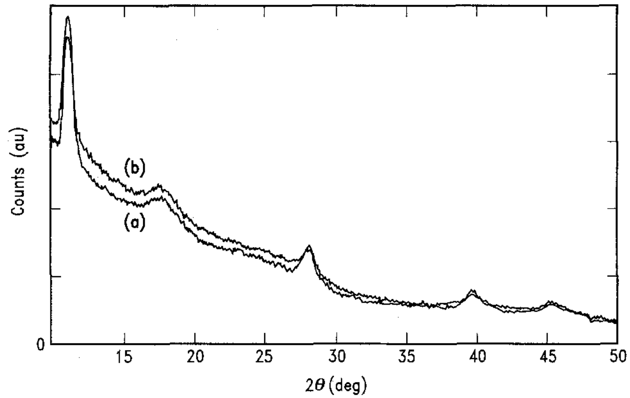

Fig. 8. WAXD transmission patterns of BPDA-PDA polyimides, prepared from the precursors (a) poly(amic ethyl ester) and (b) poly(amic acid). Film thicknesses of the free standing films were 16 μm

peaks. In accordance with the results of BPDA-PDA from poly(amic acid) in ref. [19], the four sharp peaks can be designated as *00l* peaks. (004, 00,10, 00,14, and 00,16), while the broader peak at 18 degrees (2Θ) is the 110 reflection. The WAXD transmission peaks of BPDA-PDA are nearly independent of the precursors used. The large differences between transmission and reflection pattern exhibit a strong in-plane molecular orientation for both BPDA-PDA polyimides. According to WAXD, the investigated PMDA-PDA as well as BPDA-PDA polyimides are isotropic in the film plane.

Conclusions

Thin films of rigid PMDA-PDA and semi-rigid BPDA-PDA polyimides, prepared by thermal imidization of two different precursors, were investigated. By characterizing the optical and thermo-mechanical properties as well as the chain orientation, the influence of the chemical structure and precursor nature on structure/property relationships was studied. According to optical waveguide experiments, the investigated polyimides exhibit an extraordinarily large anisotropy in the refractive indices, with the larger values observed for semi-rigid BPDA-PDA, which is quite surprising. From the optical results, no significant influence of the precursors on the refractive indices and hence molecular orientation is seen. In TMA experiments the investigated polyimides show the expected high temperature resistance and very low coefficients of the thermal expansion (CTE). In this regard, the molecular orientation, as indicated by the anisotropy of refractive indices, does not correlate well the variations of CTE of the various precursors. According to DMTA measurements in the temperature range from 25° to 400 °C only a small change of the storage modulus is found for the rigid PMDA-PDA structure, with larger changes in the storage modulus for the semi-rigid BPDA-PDA structures. BPDA-PDA based polyimides show a softening in the temperature range from 325° to 360 °C, with the larger loss tangent, tan δ, for BPDA-PDA polyimide derived from the poly(amic ethyl ester). WAXD investigations provide a large anisotropy in the supermolecular structure of PMDA-PDA as well as BPDA-PDA. Parallel to the film surface the structure is isotropic. Molecular chains are highly aligned in the plane of the film with well-defined monomeric repeat layers, analogous to smectic states, but the lateral order is rather low. A better lateral packing of the molecular chains was found for the polyimides prepared from poly(amic ethyl ester) precursors.

It should be emphasized that although the BPDA-PDA is not a rigid rodlike polymer by itself [19], its molecular orientation in thin films as reflected in the optical anisotropies and the CTE can be as high as that for rigid PMDA-PDA films. This indicates that the BPDA-PDA chains in films, with no solvents, assume predominantly rigid rodlike conformations. Such a drastic conformational ordering is in agreement with theoretical predictions for semiflexible chains in neat bulk states [20, 21]. However, the fact that BPDA-PDA is a semi-rigid chain is still manifested by the slight softening at high temperatures above ca. 325 °C and also by the larger CTE (18 ppm/°C) exhibited by ester derived films. This seems to reflect the presence of some (not rodlike) conformational defects, the details of which depend on the precursor. In this regard, the lack of correlations of WAXD results to CTE's is also consistent with the important contributions of conformational defects, since WAXD reflects solely the packing order of ordered chain segments.

Acknowledgement

The authors would like to thank H. Truong for carrying on the TGA measurements and R. S. Swope and G. L. Gorman for the WAXD measurements. We also thank B. Fuller for assistance with the DMTA measurements, IBM Germany for granting the postdoctoral fellowship to U. Goeschel, and IBM Korea for providing financial assistance to H. Lee.

References

1. Sroog CE (1976) J Polym Sci Macrom Rev 11:161
2. Numata S, Kinjo N (1988) Poly Eng Sci 28:906
3. Tummala RR, Rymaszewski EJ (1989) Microelectronics Packaging Handbook, Van Nostrand-Reinhold, New York, Chapter 1
4. Czornyj G. Chen KR, Prada-Silva G, Arnold A, Souleotis H, Kim S, Ree M, Volksen W, Dawson D, DiPietro R (1992), 42nd Electronic Components and Technology Conference, 682
5. Volksen W, Yoon DY Hedrick JL, Hofer D (1991) Mat Res Soc Symp Proc 227:23
6. Volksen W and Cotts PM (1984) Polyimides: Synthesis, Characterization, and Applications, Mittal KL, Editor, Plenum Press, New York, Volume 1:163
7. Nishizaki S, Moriwaki T (1967) J Chem Soc Japan 71:1559
8. Bell VL, Jewell RA (1967) J Polym Sci Part A-1, 5:3043
9. Herminghaus S, Boese D, Yoon DY, Smith BA (1991) Appl Phys Lett 59:104
10. Swalen JD (1986) J Molec Electron 2:155
11. Boese D, Lee H, Yoon DY, Swalen JD, Rabolt J (1992) J Polym Sci Polym Phys 30:1321
12. Swalen JD, Santo R, Take M, Fischer J (1977) IBM J Res Dev 21:168
13. Prest WM, Jr, Lucas DJ (1980) J Appl Phys 51:5170
14. Senturia D, Noe SC, Pan JY (1991) Mat Res Soc Symp Proc 227:167
15. Russell TP, Gugger H, Swalen JD (1983) J Polym Sci: Polym Phys 21:1745
16. Rojstaczer S, Ree M, Yoon DY, Volksen W (1992) J Polym Sci Polym Phys 30:133
17. Smith TL, Kim CS (1991) Mat Res Soc Symp Proc 227:219
18. Ree M, Nunes TL, Chen KR, Czornyj G (1991) Mat Res Soc Symp Proc 227:211
19. Yoon DY, Depero LE, Parrish W, Ree M (1991) Mat Res Soc Symp Proc 227:387
20. Yoon DY, Flory PJ (1989) Mat Res Soc Symp Proc 134:11
21. Yoon DY, Baumagartner A (1984) Macromolecules 17:2864

Received May 25, 1994;
accepted July 1, 1994

Authors' address:

D. Y. Yoon
IBM Research Division
Almaden Research Centre
650 Harry Road
San Jose, California 95120-6099, USA