

FLUORINATED POLYIMIDES : STRUCTURE - PROPERTY RELATIONSHIPS AND APPLICATIONS AS AN OPTICAL MATERIAL

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ABSTRACT

Optical properties of fluorinated and perfluorinated polyimides are reported, and their structure-property relationships are discussed in order to apply these materials to the optical components needed in the future telecommunication systems. The partially fluorinated and perfluorinated polyimides developed by the authors show high transparency and small birefringence in the near-IR region. These are due to the low contents of hydrogen atoms and the three dimensional molecular structure. The glass transition temperatures of these materials are sufficiently high compared to the soldering temperature. Optical waveguides and optical waveplates were fabricated using fluorinated polyimides, and their performance are reported.

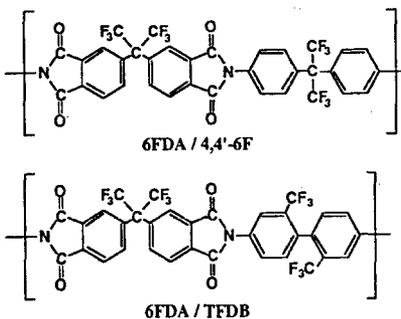
INTRODUCTION

Polymers are expected to be used as media for transmitting near-infrared light in optical communication applications such as waveguides in opto-electronic integrated circuits (OEIC) and in multichip interconnections^{1,2}. The current manufacturing process for ICs and multichip modules includes soldering at 270°C and short-term processes at temperature of up to 400°C. Polymeric materials for optical applications should therefore have high thermal stability as well as high transparency at the wavelengths of optical communications (WOC), 1.0-1.7 μm . Conventional waveguide polymeric materials, such as poly(methyl methacrylate), polystyrene, or polycarbonates, do not have such thermal stability. In addition, their optical losses at the WOC are much higher than in the visible region (0.4-0.8 μm), because carbon-hydrogen (C-H) bonds harmonically absorb infrared radiation. Several types of C-H bonds - those in methyl and methylene groups - give broad and strong absorption peaks in the infrared region. Although the

wavelengths currently used for long distance optical communication, 1.3 and 1.55 μm , are located in what are called *windows*, absorption peaks originating from C-H bonds increase the optical losses at these wavelengths.

Polyimides, on the other hand, have been investigated as optical waveguide materials because of their excellent thermal, chemical and mechanical stability³⁻⁵. Although the systematic studies on colorless polyimides were carried out by St.Clair et al.^{6,7}, the relationships between the molecular structure

and the optical properties needed for opto-electronics - absorption loss, refractive index, and birefringence - have not been clarified. Reuter et al. at IBM first reported that optimally cured partially fluorinated polyimides (6FDA/4,4'-6F) can be used to decrease optical losses below 1 dB/cm in the visible region (at 0.63 μm), and that these losses are stable at temperatures up to 200°C⁵. In 1989, we found that a novel fluorinated polyimides (6FDA/TFDB) also show high transparency in the visible region as well as low dielectric constants, low refractive indices, and low water absorption⁸. We started the development of a series of fluorinated polyimides using TFDB as a diamine⁹⁻¹².



OPTICAL PROPERTIES OF FLUORINATED POLYIMIDES

Table 1 summarizes the optical loss measured at 0.63 μm and the refractive indices of polyimide films formed on silicon substrates. Optical loss in the visible region is caused by electronic transition which is closely related to the inter- and intra-molecular charge transfer (CT). According to the CT theory, the electronic transition energy from the HOMO located around the imide-nitrogen to the LUMO located around the carbonyl carbons should be determined from the electron-donor property of diamine and the electron-acceptor property of

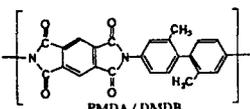
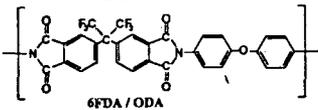
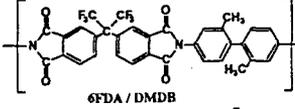
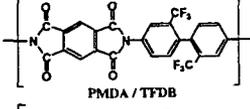
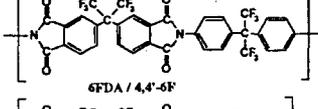
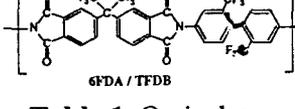
Polyimide	Optical Loss (dB/cm)	Cure Temp. (°C)	Refrac. Index (589nm)
 PMDA / DMDB	36	300	1.723
 6FDA / ODA	10	300	1.598
 6FDA / DMDB	5.5	350	-
 PMDA / TFDB	4.3	350	1.615
 6FDA / 4,4'-6F	3.0	300	1.545
 6FDA / TFDB	0.7	350	1.549

Table 1 Optical properties of polyimides.

dianhydride. We have reported that the electron-donor properties of diamines can be quantitatively estimated by ^{15}N NMR chemical shifts (δ_{N}), and we identified the orders of δ_{N} for a series of diamines (Fig.1)¹³. The larger δ_{N} of fluorinated diamines indicates their low electron-donor properties. This coincides with the fact that the polyimides prepared from fluorinated diamines show low optical loss.

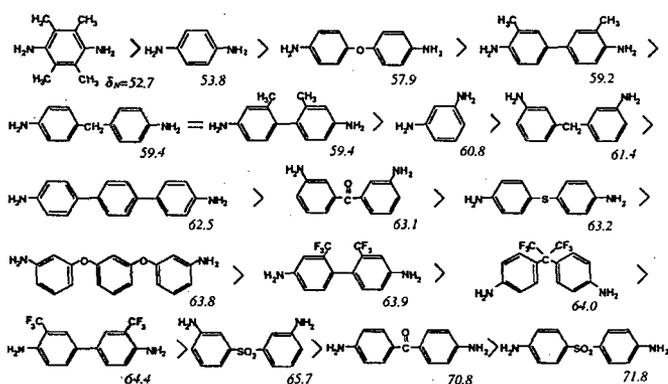


Fig.1 Aromatic diamines arranged in order of amino group ^{15}N NMR chemical shift

PROPERTY CONTROL BY COPOLYMERIZATION^{10,14}

Even though the fluorinated polyimides have attractive thermal and optical properties, most of them require some degree of modification to tailor those properties for specific applications. Increase in fluorine content generally leads to lower-dielectric constant, higher water resistance, higher optical transparency, and lower refractive index. On the other hand, lower thermal expansion and higher thermal stability can be attained by introducing more rigid-rod structure. Copolymerization of two different types of polyimides, 6FDA/TFDB and PMDA/TFDB, gives a good example. The higher content of 6FDA fosters high fluorine content and three dimensional molecular structure, while fluorine-free PMDA enhances rigid-rod structure characteristics. Figs. 2 and 3 show that the thermal expansion coefficient and the refractive indices can be precisely controlled by changing the 6FDA/TFDB content.

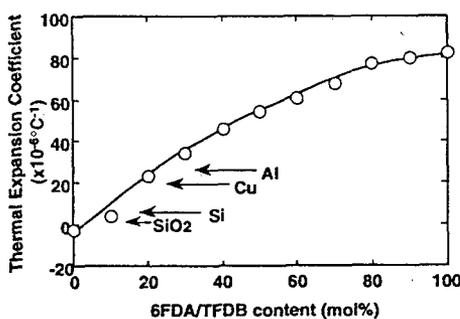
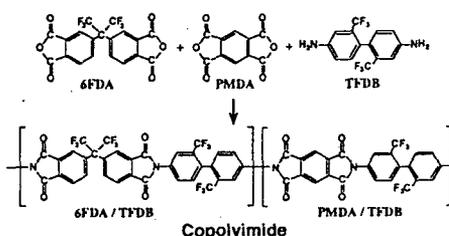


Fig.2 CTE of fluorinated copolyimide.

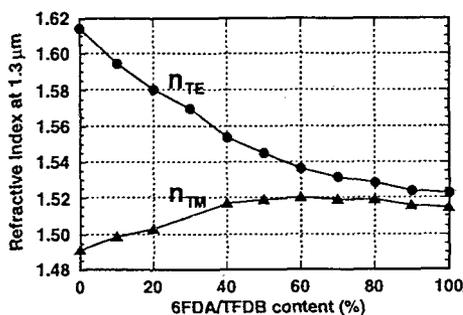


Fig.3 Refractive indices of fluorinated copolyimide.

SYNTHESIS AND PROPERTIES OF PERFLUORINATED POLYIMIDES¹⁵⁻¹⁷⁾

As described above, the optical loss at the WOC is caused by the harmonic absorption of C-H bond stretching. Polyimides also have some absorption peaks in the near-infrared region that originate from the C-H bonds in their phenyl groups. Since the wavelengths for the fundamental stretching vibrations of C-F bonds are about 2.8 times longer than that of C-H bond, the losses in the near-infrared region can be appreciably reduced by substituting fluorine for hydrogen atoms. The combination of low optical losses over the entire WOC and high thermal, chemical, and mechanical stability must therefore be attained by the perfluorination of polyimides.

Table 2 lists the properties of perfluorinated polyimides first synthesized by the authors along with those of partially fluorinated and unfluorinated polyimides. Because of the flexible structure of the 10FEDA component, the polymer decomposition temperature and T_g of perfluorinated polyimides are slightly lower than those of conventional polyimides. The thermal stability of these films is nonetheless high enough to withstand the manufacturing process of optoelectronic devices. Their dielectric constants (ϵ) at 1kHz and average refractive indices are as low as those of the partially fluorinated polyimides.

This is because the fluorine contents of perfluorinated polyimides are comparable to those of partially fluorinated polyimides. The birefringence of perfluorinated polyimides is relatively small. This originates from the steric effect between perfluorinated aromatic rings and from a number of bent structures like an ether, a thioether and a meta-phenylene

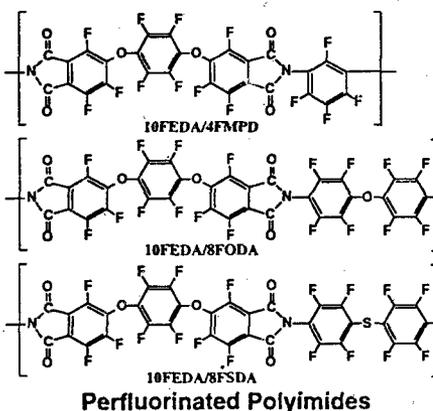


Table 2 Properties of perfluorinated, fluorinated, and unfluorinated polyimide.

	Fluorine content (%)	Decomp. temp. (°C)	T _g (°C)	ϵ	\bar{n}	$n_{TE} - n_{TM}$
10FEDA/4FMPD	36.6	501	309	2.8	1.562	0.004
10FEDA/8FODA	38.4	485	300	2.6	1.552	0.004
10FEDA/8FSDA	37.7	488	278	2.6	1.560	<0.01
10FEDA/TFDB	35.1	543	312	2.8	1.569	0.009
6FDA/TFDB	31.3	553	327	2.8	1.548	0.006
PMDA/TFDB	22.7	613	>400	3.2	1.608	0.136
PMDA/ODA	0	608	>400	3.5	1.714	0.088

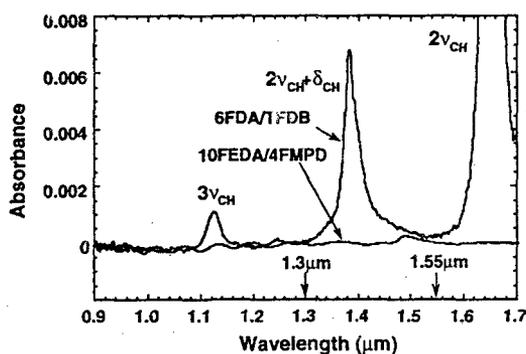


Fig. 4 Absorption spectra of fluorinated and perfluorinated polyimides.

linkage. As shown in Fig. 4, the perfluorinated polyimide exhibits no substantial absorption peaks in the near-IR region.

OPTICAL WAVEPLATES¹⁸⁻²⁰⁾

Calcite and quartz are commonly used for optical polarization components, such as waveplates, polarizers, and beam splitters. However, their birefringence cannot be changed and they are difficult to make into thin plates or small components. In-plane birefringence (Δn) of fluorinated polyimides were investigated by uniaxially drawing of poly(amic acid) films during curing with a constant load (Fig. 5). The Δn of the rod-like polyimide (PMDA/TFDB) can be controlled between 0.02 and 0.19 by changing the final curing temperature. A polyimide half-waveplate at 1.55 μm , only 14.5 μm thick, which is 6.3 times as thin as a quartz waveplate, was prepared. The excess loss of mode converters with this waveplate were about 1/20 of that with a quartz waveplate (Fig. 6). Its retardation was retained after annealing at 350°C for 1 hour.

SINGLE-MODE OPTICAL WAVEGUIDES^{21,22)}

Optical waveguides are indispensable for transmitting and processing optical signals in optoelectronic devices. Waveguides consist of a high-refractive-index core (diameter $\approx 8 \mu\text{m}$) embedded in a slightly lower refractive-index cladding to assure single-mode operation and low optical loss. We have fabricated single-mode waveguides using fluorinated polyimides with a low loss ($< 0.3 \text{ dB/cm}$) at 1.3 μm .

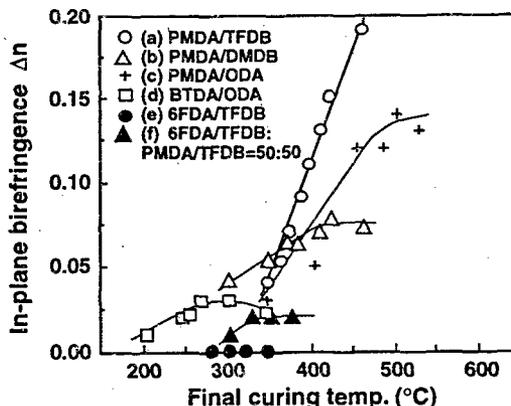


Fig. 5 In-plane birefringence of polyimides versus final curing temperature.

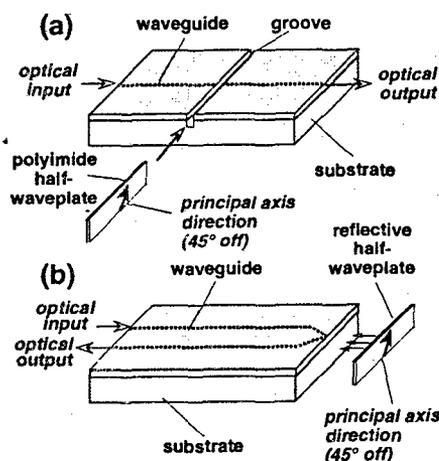


Fig. 6 Two types of mode convertor with thin polyimide waveplates.

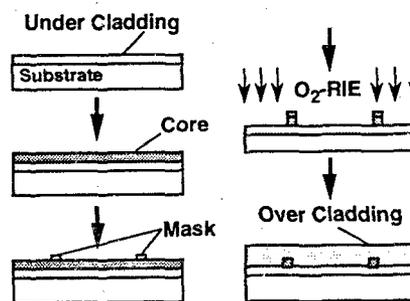


Fig. 7 Fabrication process of single-mode polyimide optical waveguides.

Fig. 7 outlines the sequence of waveguide fabrication. The refractive indices of the core and the cladding were precisely controlled (± 0.001) by the copolymerization technique. The increase in optical loss is less than 5% after heating at 300°C for 1h exposure to 85% relative humidity at 85% for 24h.

SUMMARY

Fluorinated and perfluorinated polyimides exhibit high transparency in the near-IR region, low dielectric constants, and low water absorption. The refractive index and birefringence can be precisely controlled in wide ranges by changing molecular structure and/or curing conditions. These characteristics indicate that the fluorinated and perfluorinated polyimides are promising materials for optical communication applications.

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