

Synthesis of Fluorinated Polyimides and Their Application to Passive Optical Waveguides

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ABSTRACT: Fluorinated and chlorofluorinated polyimides with high thermal stability and low optical absorption loss in the optical communication wavelengths of 1.3 and 1.55 μm were investigated for low-loss passive waveguide applications. These polyimides were prepared from pyromellitic dianhydride (PMDA) with 1,4-bis-[4-amino-2-(trifluoromethyl)phenoxy]tetrafluorobenzene (ATPT), 1,4-bis-[4-amino-2-(trifluoroethyl)phenoxy]benzene (ATPB), and 1,3-bis-[4-amino-2-(trifluoromethyl)phenoxy]-4,6-dichlorobenzene (ATPD). Control of the refractive indices of the polymers was achieved from 1.5397–1.5671 for TE polarization and 1.5239–1.5513 for TM polarization at 1.55 μm by copolymerization of PMDA/ATPT and PMDA/ATPB. As the amount of PMDA/ATPT was increased, the refractive indices of the polymers were decreased. Rib-type optical waveguides were fabricated using these fluorinated polyimides. These waveguides exhibited a low propagation loss of less than 0.5 dB/cm at 1.55 μm . © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 2172–2177, 2000

Key words: fluorinated polyimides; reflective index; low optical loss; optical telecommunication; optical waveguide

INTRODUCTION

Polymeric materials are of great interest for applications in optical telecommunications such as optical waveguides and optical interconnections due to their ease of processing and relatively low cost compared to silica-based materials.^{1–3} Although these materials have potential advantages for optical applications, there is a need for improvement in some properties such as high thermal property, low thermal stress, and low absorption loss at the optical telecommunication wavelengths of 1.3 and 1.55 μm . It is known that the loss of polymeric materials at near-infrared (IR) wavelengths is attributed mainly to absorption from vibrational overtones of the carbon–hydrogen (C–H) bond, and this

loss can be reduced appreciably by the substitution of hydrogen atoms with deuterium or fluorine.^{4–6} Thus, it is reported that fluorinated polymers are considered to be one of the potential candidates for optical applications because they have excellent optical transparency at the optical telecommunication wavelengths.^{7–9} Among these polymers, fluorinated or perfluorinated polyimide has been considered for real-device applications due to its excellent thermal, mechanical, and optical properties. In this article, we describe the synthesis and characterization of a series of fluorinated and chlorofluorinated polyimides which exhibit good thermal stability, a controllable refractive index, and low optical loss in the optical communication wavelengths of 1.3 and 1.55 μm . The fabrication of waveguides by using these polyimides and characterization of their optical properties are also demonstrated.

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EXPERIMENTAL

Materials

Tetrafluoro-1,4-hydroquinone (Apollo Scientific), 2-chloro-5-nitrobenzotrifluoride (Aldrich), potassium carbonate (Aldrich), tetra-*n*-butylammonium chloride (Fluka), and 10% Pd/C (Kojima Chem.) were used as received. Hydroquinone (Kanto Chem.) and pyromellitic dianhydride (PMDA; Aldrich) were recrystallized from toluene and acetone, respectively. 4,6-Dichlororesorcinol (Aldrich) was purified by sublimation under reduced pressure prior to use. *N,N'*-Dimethylacetamide (DMAc; Aldrich) was purified by distillation under reduced pressure over calcium hydride.

Monomer Synthesis¹⁰

1,4-Bis-[4-nitro-2-(trifluoromethyl)phenoxy]tetrafluorobenzene

Tetrafluoro-1,4-hydroquinone (2.76 g, 0.015 mol), 6.91 g of potassium carbonate, and 40 mL of DMAc were placed under nitrogen in a 250-mL round-bottom flask. 2-Chloro-5-nitrobenzotrifluoride (7.52 g, 0.033 mol), 0.098 g of tetra-*n*-butylammonium chloride, and 0.020 g of copper powder was then introduced into the reactor. The mixture was heated to 80°C for 17 h and then filtered to remove the copper powder. The filtered solution was precipitated in 500 mL of methanol–water (1:1 by volume). The resulting precipitate was collected by filtration and washed with 1.5 L of distilled water. After the precipitate was dissolved in tetrahydrofuran (THF), the solution was dried over magnesium sulfate. After removal of THF, the crude product was purified by recrystallization from glacial acetic acid. The yield was 5.51 g (65%).

¹H-NMR (acetone-*d*): δ 6.7–7.3 ppm (6H, aromatic). IR (KBr pellet): 1052 and 1234 cm⁻¹ (C—O—C), 1488 and 1333 cm⁻¹ (NO₂).

Two other nitro compounds, 1,4-bis-[4-nitro-2-(trifluoromethyl)phenoxy]benzene (yield: 72%) and 1,3-bis-[4-nitro-2-(trifluoromethyl)phenoxy]-4,6-dichlorobenzene (yield: 63%) were obtained by a procedure similar to those mentioned above.

1,4-Bis-[4-amino-2-(trifluoromethyl)phenoxy]tetrafluorobenzene (ATPT)

Seven grams of 1,4-bis-[4-nitro-2-(trifluoromethyl)phenoxy]tetrafluorobenzene, 0.7 g of 10% Pd/C, and 60 mL of THF were introduced into a one-neck round-bottom flask. After the flask was evacuated,

hydrogen gas was injected into the reaction mixture. The above procedure was repeated several times and the reaction mixture was stirred for 24 h at room temperature. Then, the solution was filtered through celite to remove Pd/C. The filtered solution was poured into 200 mL of *n*-hexane to precipitate the white compound. It was dried at 50°C under reduced pressure to 4.772 g (76.3% yield).

¹H-NMR (acetone-*d*): δ 6.8–6.9 ppm (d, 2H, aromatic), (6.9–7.0 ppm (d, 2H, aromatic), (7.1–7.2 ppm (s, 2H, aromatic), and (4.9–5.0 ppm, (s, 4H, —NH₂). IR (KBr pellet): 1052 and 1260 cm⁻¹ (C—O—C), 3400, 3490 cm⁻¹ (NH₂).

Two other amine compounds, 1,4-bis-[4-amino-2-(trifluoromethyl)phenoxy]benzene (ATPB; yield: 75.5%) and 1,3-bis-[4-amino-2-(trifluoromethyl)phenoxy]-4,6-dichlorobenzene (ATPD; yield: 52.6%) were obtained by a procedure similar to those mentioned above.

Polymerization and Film Preparation

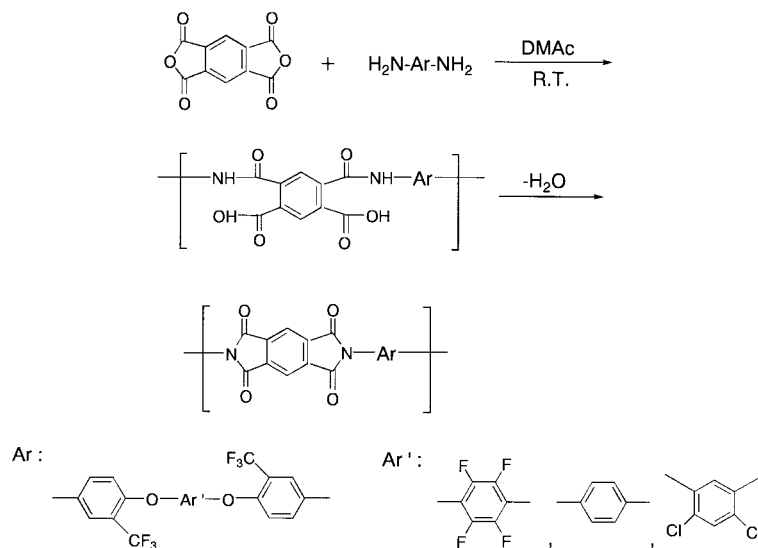
Fluorinated and chlorofluorinated polyimides were prepared according to a general reaction as shown in Scheme 1. {Scheme 1} Polymerizations were carried out under a nitrogen atmosphere by adding a stoichiometric amount of diamine and dianhydride in DMAc at room temperature. A series of copolyimides were prepared from the two amines, ATPT and ATPB, with PMDA. The content of ATPT was varied (20–80 mol % based on ATPB). The resulting poly(amic acid) solutions were filtered through a 1.0-μm Teflon filter and then spun-coated onto a silicon wafer, followed by curing at 80°C/2 h, 160°C/1 h, 250°C/0.5 h, 300°C/0.5 h, and 350°C/0.5 h.

Waveguide Fabrication

Rib-type optical waveguides were fabricated by spin coating an undercladding and a core polymer on an oxidized silicon substrate. Core ridges were then formed by conventional photolithography and dry etching using a plasma etcher. The waveguides were fabricated by covering the core ridges with an overcladding polymer by spin coating.

Measurements

A Varian Gemini 200 was used for the ¹H-NMR measurements. A Perkin–Elmer DSC Pyris 1 was used to obtain the glass transition temperatures (*T*_g) of the polymers at a heating rate of 20°C/min. Thermogravimetric analyses (TGA) were carried



Scheme 1

on a DuPont TGA 2950 thermal analyzer at a 10°C/min heating rate in a nitrogen atmosphere. UV transparencies were measured by a Hewlett-Packard HP8453 spectrophotometer. Refractive indices of the polymer films were measured using a Metricon 2010 prism coupler using light from a 1.3- μm laser diode and a 1.55- μm laser diode. The inherent viscosities of the poly(amic acid) samples were measured with an Ubbelohde viscometer using DMAc as a solvent. Near-infrared spectra of the polyimide films (180 μm thick) were recorded on an ATI Mattson Infinity FTIR spectrometer. The near-field mode pattern and loss of the waveguides were recorded using a 1.55- μm laser diode. The incident light beam was introduced to the waveguides through a single mode fiber with mode-field diameter of 10 μm . The propagation loss of the straight waveguides was measured by the cutback method.¹¹ The output beam power intensity was measured with an Anritsu optical power meter.

RESULTS AND DISCUSSION

Synthesis of Monomer

The diamines, 1,4-bis-[4-amino-2-(trifluoromethyl)phenoxy]tetrafluorobenzene (ATPT), 2,2',6,6'-1,4-bis-[4-amino-2-(trifluoromethyl)phenoxy]benzene (ATPB), and 4-bis-[4-amino-2-(trifluoromethyl)phenoxy]-2,4-dichlorobenzene (ATPD), were synthesized in two steps by the reaction of 2-chloro-5-nitrobenzotrifluoride with tetrafluorohydroquinone, hydroquinone, and 3,5-dichloronitrobenzene,

respectively, followed by reduction of the corresponding nitro compounds with hydrogen in the presence of Pd/C. The structures of the nitro and diamine compounds were confirmed by ¹H-NMR and IR. After reduction, absorption peaks from the nitro group at 1333 and 1488 cm^{-1} disappeared and peaks from the primary amine at 3400 and 3490 cm^{-1} were observed in the IR spectra. In the ¹H-NMR spectra, the primary amine signal around 4.95 ppm was observed after reduction.

Preparation of Polymers and Their Thermal Properties

Fluorinated and chlorofluorinated polyimides were synthesized from PMDA, ATPT, and ATPB. The copolyimides were prepared from the two amines, ATPT and ATPB, with PMDA. The content of ATPT was varied (20–80 mol % based on ATPB) as shown in Scheme 1. The intrinsic viscosities of the resulting poly(amic acid) were between 1.8 and 2.3 dL/g measured at 30°C in DMAc, exhibiting the high molecular weights of these polymers. The measured glass transition temperatures of three kinds of polyimides are shown in Table I. As shown in this table, T_g increases in the order of PMDA/ATPT > PMDA/ATPD > PMDA/ATPB. It seems that halogen substituents cause the decrease of the flexibility of the polymer chain (prevent rotation along the chain) and the increase of intermolecular interaction due to the increasing polarity of the polymer backbone. The thermal decomposition temperatures are shown in Figure 1. It is observed that the decomposition starts at a lower temperature

Table I Thermal Properties of the Polymers

Polymer	T_g (°C) ^a	Onset Temperature of Weight Loss (°C) ^b
PMDA/ATPT	309	522
PMDA/ATPB	292	537
PMDA/ATPD	298	495

^a Determined by DSC at a heating rate of 20°C/min in a nitrogen atmosphere.

^b Determined by TGA at a heating rate of 10°C/min in a nitrogen atmosphere.

by halogen substitution. These temperatures decrease in the order of PMDA/ATPB > PMDA/ATPT > PMDA/ATPD. This order seems to correspond to the order of the bond dissociation energies of carbon–halogen (C–X) bonds.¹²

Optical Properties

Optical Transparency in the Near-Infrared (NIR) Region

Whereas the electronic transition causes the absorption in the UV region, the harmonics and their coupling of the stretching vibration of chemical bonds cause the absorption in the near-infrared region. The carbon–hydrogen (C–H) and oxygen–hydrogen (O–H) bonds are reported to strongly affect the absorption in the near-infrared region.¹³ The low absorption in both the 1.3- and 1.55- μm wavelengths, which are used in optical

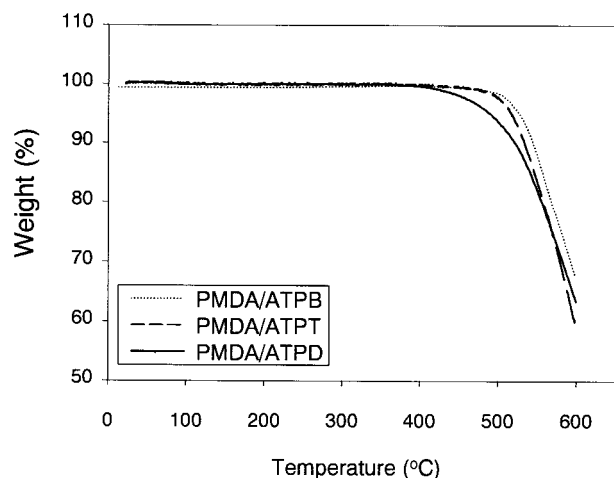


Figure 1 TGA thermograms of polyimides with a heating rate of 10°C/min in a nitrogen atmosphere.

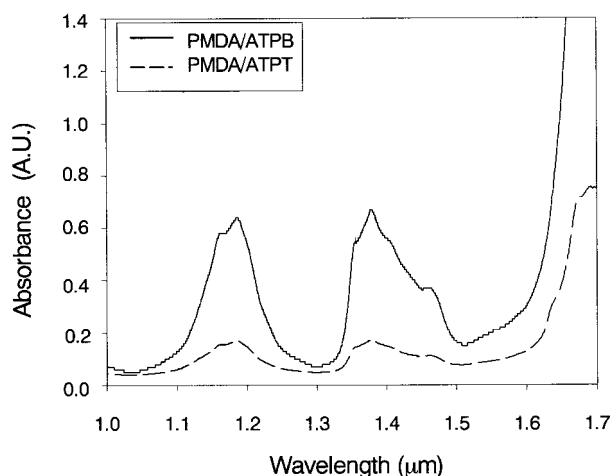


Figure 2 Near-infrared spectra of the polyimides.

communications, is an important consideration in using these polymers for optical devices. It is also reported that the absorption due to C–H bonds can be reduced by the replacement of hydrogen in the C–H bonds to heavier atoms such as fluorine (F), chlorine (Cl), and deuterium (D).^{14,15} The absorption in the near-infrared region, therefore, is strongly related to the number of C–H bonds in the polymer. The smaller the number of C–H bonds in the polymer, the lower the absorption in the near-infrared region. Figure 2 shows the near-infrared absorption spectra of PMDA/ATPB and PMDA/ATPT polyimide films. As expected, the absorption of PMDA/ATPT is smaller than that of PMDA/ATPB due to the smaller number of C–H bonds in this material.

Refractive Index and Birefringence

The in-plane (n_{TE}) and out-of-plane (n_{TM}) refractive indices and the birefringence (the difference between n_{TE} and n_{TM}) of the films were determined with a prism coupler.¹⁶ These are shown in Table II. The films were prepared by spin coating

Table II Refractive Indices of Polyimide Film

Polyimides	n_{TE}	n_{TM}	Birefringence ($n_{TE} - n_{TM}$)
PMDA/ATPT	1.5397	1.5239	0.0158
PMDA/ATPB	1.5671	1.5513	0.0158
PMDA/ATPD	1.5727	1.5670	0.0057

^a Determined by Metricon 2010 prism coupler using a 1.55- μm laser diode.

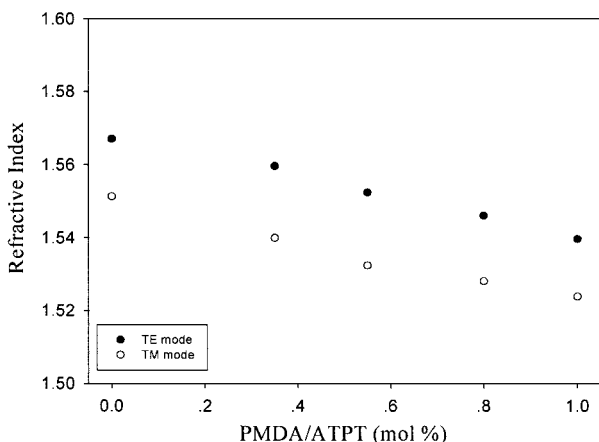


Figure 3 Refractive indices of fluorinated copolyimides at 1.55 μm .

poly(amic acid) solutions onto silicon wafers and then backed to 350°C under a nitrogen atmosphere. The film thicknesses were between 10 and 12 μm . It is known that the refractive indices, and, therefore, the birefringence, in polyimide films are affected by several factors. These factors include the chain flexibility and linearity, geometry of the repeat units, and polarizability and orientation of the bonds in the polymer backbone. As shown in Table II, the n_{TE} is larger than is n_{TM} in every case. This is due to the rigid aromatic molecules, which tend to align in parallel with the film surface during the film processing. Due to this ordering, light travels slower (higher refractive index) in the in-plane direction compared with the out-of-plane direction. The n_{TE} 's and n_{TM} 's of films tend to increase in the order of PMDA/ATPD > PMDA/ATPB > PMDA/ATPT, which is consistent with the increasing order of polarizability. It is known that refractive indices of fluorine-containing polymers are smaller than those of unfluorinated polymers due to the smaller polarizability of the carbon–fluorine bond (C–F) compared to that of the carbon–hydrogen (C–H) bond. Because the polarizability of car-

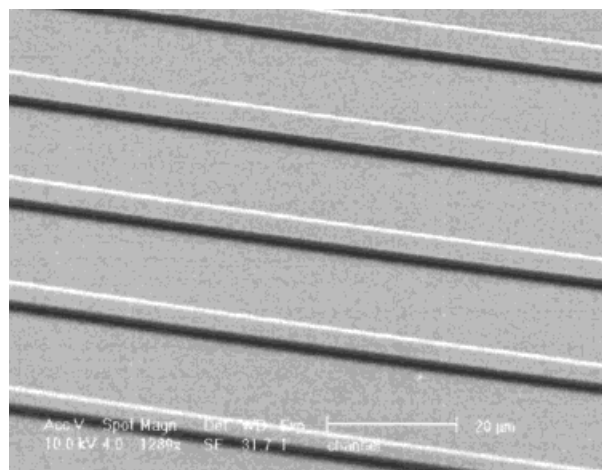
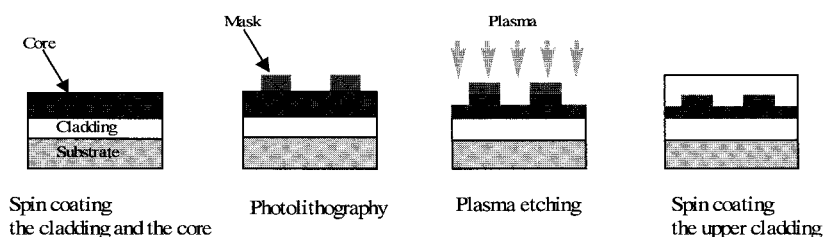


Figure 4 SEM image of core ridges.

bon–chlorine (C–Cl) is larger than that of the C–H bond,¹⁷ and light travels slower through more polarizable bonds, the refractive index of the chlorine-containing polymer, PMDA/ATPD, is the largest among the polymers. Note that the birefringence of PMDA/ATPD is the smallest. This is attributed to the kink structure of this polymer, and this structure prevents in-plane orientation.

Refractive Index Control of Polymers

Because optical waveguides consist of a light-carrying core (high refractive index) and a cladding (low refractive index), one of the important requirements for an optical polymer is precise control of the refractive indices for them. It was reported that the copolymerization of different fluorine content-containing monomers provides good methodology to control the refractive indices of polymers for waveguide applications. We copolymerized PMDA with two different diamines, ATPT and ATPB. As shown in Figure 3, the refractive indices of the polymers decreased linearly as the amount of the more fluorinated diamine, ATPT, increased to 1.55 μm for both in-plane (TE)



Scheme 2

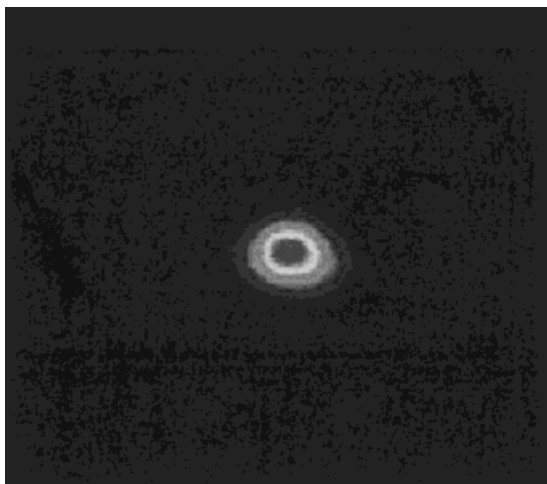


Figure 5 Near-field mode pattern for TE polarized light at 1.55 μm .

and out-of-plane (TM) polarizations. We were able to control the refractive indices of the polymers in the range of 1.5397–1.5671 for TE polarization and 1.5239–1.5513 for TM polarization at 1.55 μm by copolymerization of PMDA/ATPT and PMDA/ATPB.

Fabrication and Characterization of Rib-Type Waveguides

Rib-type optical waveguides were fabricated by using fluorinated copolymers. An undercladding layer (PMDA/ATPT, $n_{\text{TE}} = 1.5420$, $n_{\text{TM}} = 1.5211$, and 18 μm thick) and a core layer (PMDA/ATPT: PMDA/ATPB = 4:6, $n_{\text{TE}} = 1.5597$, $n_{\text{TM}} = 1.5397$, and 4.4 μm thick) were spin-coated onto an oxidized silicon substrate. Core ridges (1.6 μm depth and 6 μm width) were then formed by conventional photolithography and dry etching. Waveguides were fabricated by covering the core ridges with an overcladding polymer (20 μm thick) by spin coating as shown in Scheme 2. Figure 4 shows a scanning electron microscopy (SEM) image of the core ridge of the waveguides. The smooth etch profile could be achieved by this plasma-etching process. The propagation loss of the straight waveguides at 1.55 μm was measured by the cutback method. Less than 0.5 dB/cm of propagation loss was measured in a 6- μm -width waveguide at 1.55 μm . Figure 5 shows the near-field mode pattern of the waveguide (6 μm width), demonstrating a single mode at 1.55 μm . Details of the waveguide structure and the performance of the optical device will be reported elsewhere.

CONCLUSIONS

The fluorinated polyimides with good thermal stability, refractive index controllability, and low optical loss at the optical telecommunication wavelengths of 1.3 and 1.55 μm were synthesized. The refractive indices of the polymers were controlled by copolymerization of PMDA with two different fluorine-containing diamines, ATPT and ATPB. The refractive indices of polymers decreased as the amount of ATPT increased and could be controlled in the range of 1.5397–1.5671 for TE polarization and 1.5239–1.5513 for TM polarization at 1.55 μm . Rib-type polymeric waveguides were prepared by using these fluorinated polyimides. These waveguides exhibited a low optical loss of less than 0.5 dB/cm at 1.55 μm .

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