

FLUORINATED PHTHALAZINONE-CONTAINING COPOLYIMIDES FOR PASSIVE OPTICAL WAVEGUIDES*

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Abstract A series of fluorinated copolyimides containing phthalazinone moieties were prepared from 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA), 3,3',4,4'-benzophenone-tetracarboxylic dianhydride (BPDA) and 2-(4-aminophenyl)-4-[4-(4-aminophenoxy)phenyl]-2,3-phthalazin-1-one (DHPZ-2NH₂) for making polymeric optical waveguides. The resulting copolymers containing 0–50 mol% BPDA/ DHPZ-2NH₂ show good solubility and are soluble in some organic polar aprotic solvents. The copolyimides also present excellent thermal stability. These polymers possess high glass transition temperature higher than 603 K and high decomposition temperature above 742 K determined by differential scanning calorimetry and thermogravimetric analysis, respectively, under a nitrogen atmosphere. Their refractive indices could be controlled by varying the ratio of 6FDA and BPDA in the copolymer from 0.5 to 1.0, and the in-plane refractive indices (n_{TE}) range from 1.6366 to 1.6668 and the out-of-plane refractive indices (n_{TM}) from 1.6024 to 1.6280 at 632.8 nm. The polymers birefringence (0.0342–0.0388) is almost independent of the 6FDA content of copolymer, which indicated that the phthalazinone-containing copolyimides could be suitable to fabricate optical waveguides possessing a low polarization dependent loss (PDL).

Keywords: Polymeric optical waveguides; Fluorinated polyimides; Phthalazinone.

INTRODUCTION

The trend toward high transmission speed, data capacity and data density in integrated circuits demands a solution to the bottleneck by virtue of the limited data rate of electric interconnects. The best approach to this problem is the use of optical interconnects with polymeric optical waveguides. Polymeric optical device for optical telecommunications have attracted a lot of attention due to their easy processibility and cost effective technology compared to semiconductor materials such as silicon. The critical requirements imposed on optical waveguide polymeric materials involve low optical loss at the optical telecommunication wavelengths of 1.3 and 1.55 μm , precise controllable refractive index and sufficient thermal stability to withstand typical fabrication processing and operation condition. It is well known that loss at near-infrared wavelengths is mainly attributed to absorption from vibrational overtones of the carbon-hydrogen bond. The substitution of hydrogen atoms with fluorine atoms in polymer's chain can appreciably reduce the intrinsic absorption loss at near-infrared (IR) wavelengths, and simultaneously improves the solubility of polymers^[1]. For the control of refractive indices of polymers, it was reported that the copolymerization of fluorinated and nonfluorinated monomers provides a good method to control the refractive indices of polymers.

Polyimides with low dielectric constant, low water absorption, low thermal expansion and high glass transition temperature are very useful for interlayer dielectrics in electronic devices such as integrated circuits. The application of polyimides to highly complex integrated optical devices and optical interconnections in planar substrate, are recently being studied, and the results show that this class of polymers is also effective in the

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field of optical communication^[2]. Fluorinated copolyimides have been considered to be one of the important candidates for optical application due to their excellent thermal, mechanical and optical properties.

Phthalazinone-containing polymers have good thermal stability and solubility in some common organic solvents^[3]. Polymers with good solubility are suitable for processing of optical devices^[4]. In this paper, we describe a series of fluorinated polyimides containing phthalazinone moieties, which exhibit good thermal stability, a controllable refractive index and good solubility.

EXPERIMENTAL

Reagents

4,4'-(Hexafluoroisopropylidene)diphthalic anhydride (6FDA) and 3,3',4,4'-benzophenone-tetracarboxylic dianhydride (BPDA) were obtained from Hoechst Chinese Ltd., and used as received. 2-(4-Aminophenyl)-4-[4-(4-aminophenoxy)phenyl]-2,3-phthalazin-1-one (DHPZ-2NH₂) was synthesized according to the literature^[5]. *N*-methyl-2-pyrrolidinone (NMP) and *m*-cresol were dried by shaking with 0.3 nm molecular sieves, and then purified by distillation under reduced pressure. Other common organic substances were reagent grade and used as received unless otherwise stated.

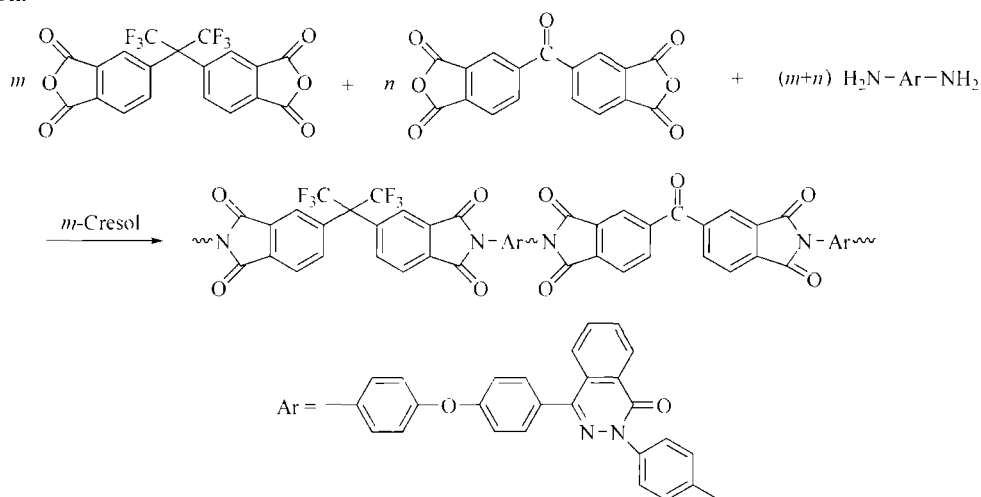
Instrumentation and Procedures

The glass transition temperatures (T_g s) were determined on a Perkin-Elmer 7 series thermal analysis system with a heating rate of 10 K/min under nitrogen (50 mL/min). Two consecutive runs were performed for each polymer (with normal cooling between scans), and the T_g s was taken from the second scan at the midpoint of the change in the slope of the baseline. Thermogravimetric analysis (TGA) of the polymer samples were also determined by a Perkin-Elmer 7 series thermal analysis system running from 298 K to 973 K at a heating rate of 10 K/min under dried nitrogen atmosphere. Intrinsic viscosities were measured in NMP at 298 K, using an Ubbelohde dilution viscometer.

Refractive indices of the polymers were measured by using a Metricon M2010 Prism Coupler. To prepare films on the silicon substrates, NMP was used as the solvent to give 15–20 wt% solutions that were filtered by 0.45 μ m syringe filters. Films of 3–5 μ m thick were prepared by spin coating on silicon disks. These films were treated at 473 K for 20 min followed by cooling spontaneously.

Preparation of Copolyimides

The copolyimides for this study were prepared by the reaction shown in Scheme 1. 6FDA (0.4602 g, 1 mmol), BPDA (0.3225 g, 1 mmol) and DHPA-2NH₂ (0.8406 g, 2 mmol) were added into a three-necked round bottom flask charged with *m*-cresol (13 mL). The reaction mixture was vigorously stirred under the protection of nitrogen atmosphere at room temperature for 1 h. A catalytic amount of isoquinoline (5 drops) was dropped into the solution.



Scheme 1 The synthesis of phthalazinone-containing copolyimides

The reaction solution was heated from room temperature to 473 K, and maintained at 473 K for more than 20 h. During this period of time, about 5 mL *m*-cresol was distilled off. Then the viscous solution was cooled to about 373 K and poured into 120 mL alcohol slowly. The polymer was purified from NMP twice, and then washed with methanol using a Soxhlet extractor overnight. After dried under high vacuum at 423 K for 24 h, then 523 K for 2 h, the polymer (1.45 g, yield 91%) was obtained as white powder.

RESULTS AND DISCUSSION

Solubility Studies

6FDA/DHPZ-2NH₂ homopolyimide can be soluble in organic polar solvents such as chloroform, 1,1,2,2-tetrachloroethane (TCE), *N,N*-dimethylformamide (DMF), tetrahydrofuran (THF) and dimethylsulfoxide (DMSO), but BPDA/DHPZ-2NH₂ homopolyimide is insoluble in any solvent. The copolymer containing more than 50 mol% BPDA/DHPZ-2NH₂ units is insoluble in solvent for polymerization (*m*-cresol). Thus the solubility differences result from the BPDA/DHPZ-2NH₂ content of 0–50 mol% of chain of polyimide. The final copolyimides can be completely soluble in DMF, NMP at room temperature, which can be fit for multilayer spin-coating processing of optical devices.

Thermal Stability

The current manufacturing process of polymeric optical waveguides for integrated optical circuits (IOCs) includes soldering at 533 K and short-term processes at 673 K. Thus waveguide polymeric materials should have high thermal stability, *i.e.*, high glass transition temperature (T_g) and high decomposition temperature (T_d). Table 1 shows the T_g and T_d of copolyimides obtained. The T_d defined as 5% weight loss in a nitrogen atmosphere, decreases with increasing 6FDA/DHPZ-2NH₂ content. All copolymers have T_d above 742 K.

Because no high weight molecular copolymers containing more than 50 mol% BPDA/DHPZ-2NH₂ units, were obtained by one-step polymerization, due to poor solubility in *m*-cresol. The T_g of copolymers could not be exhibited in differential scanning calorimetry. Table 1 shows that the T_g s of all listed copolyimides are higher than 603 K. The effect of fluorine content on the T_g s of copolymers shows the same trend as the T_d s. The copolymer containing 50 mol% BPDA/DHPZ-2NH₂ units has the highest T_g (637 K). The above results indicate that our copolymers have excellent thermal stability and meet the requirement for manufacturing process of IOCs.

Table 1. Thermal properties of copolyimides

Copolymers	6FDA : BPDA	η (dL g ⁻¹)	T_g (K)	T_d (K)
1	1:0	0.90	603	742
2	3:1	0.89	612	751
3	2:1	0.73	615	752
4	1:1	0.60	637	758

Refractive Indices of Copolymers

The refractive indices of polymers include the in-plane refractive indices (n_{TE}) and the out-plane refractive indices (n_{TM}). The n_{TE} and n_{TM} of copolymers changes from 1.6366 to 1.6668 and from 1.6024 to 1.6280, respectively at 632.8nm with the variation of the ratio of 6FDA and BPDA from 0.5 to 1.0 in the chain of copolymers (as shown in Fig. 1). Figure 1 also shows how the fluorine content affected the refractive indices of our copolyimides. Both refractive indices decrease linearly with increasing 6FDA/DHPZ-2NH₂ content due to the increase of fluorine content. The atomic refraction of fluorine is lower than that of hydrogen and will therefore reduce the index of refraction of the polymers.

A major optical property that influences transparency is the birefringence, the refractive indices difference between n_{TE} and n_{TM} . As shown in Fig. 1, the birefringence of polyimides, $\Delta n = n_{TE} - n_{TM}$, is in the range of 0.0342–0.0388, which is almost independent of the 6FDA content of copolymer. This means that the difference between the refractive indices of the cladding and core for the TE polarization (Δn_{TE}) is not very different from

that for TM polarization (Δn_{TM}). This is very advantageous for reducing the polarization-dependent optical loss of the waveguides that is caused by large difference between Δn_{TE} and Δn_{TM} . The above results indicate that the refractive indices of phthalazinone-containing copolyimides can be controlled by the copolymerization of 6FDA/DHPZ-2NH₂ and BPDA/DHPZ-2NH₂, without causing either further optical loss or changing the birefringence.

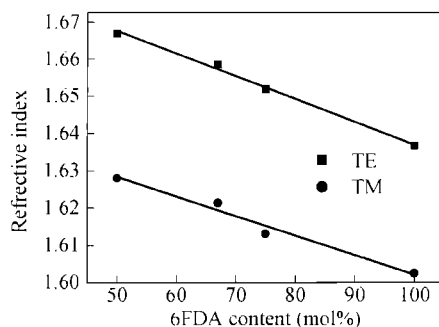


Fig. 1 Refractive indices versus 6FDA content of copolyimides at 632.8 nm and 293 K

CONCLUSION

The fluorinated copolyimides containing phthalazinone moieties for polymeric optical waveguide devices were successfully synthesized. These polymers can easily make into thin films by spin-coating resulting from their excellent solubility. They show high thermal stability. The refractive indices of copolymers could be controlled by adjusting the relative content of 6FDA and BPDA in the copolymer. The birefringence of copolymers is from 0.0342 to 0.0388, which indicate that phthalazinone-containing copolyimides are suitable to fabricate optical waveguides possessing a low polarization dependent loss. This research shows the potential applicability of copolyimides containing phthalazinone moieties in the field of polymer passive optical waveguides.

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