Synthesis and Characterization of Fluorinated Poly(phenylmaleimide-*co*-pentafluorophenylmaleimide) for Optical Waveguides

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Fluorinated polymaleimides with high thermal stability and low optical absorption loss in the optical communication wavelength of 1.55 µm were investigated for application in low-loss waveguide materials. The fluorinated polymaleimides were prepared from two monomers phenylmaleimide (H-PMI) and pentafluorophenylmaleimide (F-PMI). All synthesized copolymers had high thermal stability (decomposition temperature (T_d) = 380-430 °C). The refractive index of the copolymers could be tuned from 1.4969 to 1.5950 in the TE mode and from 1.4993 to 1.5932 for the TM mode at 632.8 nm by copolymerizing different weight ratios of H-PMI and F-PMI. The refractive index of the copolymers decreased with increasing F-PMI content. In addition, when the amount of F-PMI was increased, optical loss and absorption loss at 632.8 nm and 1550 nm, respectively, decreased.

Key Words : Fluorinated polymaleimide, Waveguide, Refractive index, Optical loss

Introduction

The present need for efficiently transferring data in public transport and at home necessitates novel broad-bandwidth technologies such as optical networking. The use of dense wavelength division multiplexing (DWDM) in optical networks is challenging, and component manufacturers have to design a variety of new devices that can be integrated into DWDM systems.[1] Polymeric materials are receiving increasing attention for applications in optical telecommunication devices, such as optical waveguides and optical interconnections, because they are easily processed and have a relatively low cost compared to silica-based materials.[2,3] Furthermore, polymeric materials can be deposited onto many substrates, including semiconductors, and show little dispersion in the refractive index between infrared and millimeter wavelength.[4] Therefore, polymers are ideally suited for short-distance optical interconnections and for the fabrication of multiple optical components such as splitters, combiners, multiplexers, switches, attenuators, and filters.[1,5-7]

With respect to applications in optical waveguide devices, the key requirements for polymeric waveguide materials are a low propagation loss at wavelengths of 1.3 and 1.55 mm, a small birefringence, and a high thermal stability. Many researchers have reported the synthesis of fluorinated polyimides that reduce optical loss and increase thermal stability.[9] It is commonly known that the optical loss of polymeric materials at near-infrared (NIR) wavelengths mainly originates from absorption by vibration overtones of the carbon–hydrogen (C–H) bond, which allows for its effective reduction by substituting hydrogen atoms with deuterium or fluorine.[9,10] Therefore, fluorinated polymers are considered to be potential candidates for optical applications because they possess excellent optical transparency at optical telecommunication wavelengths.[11] At the same time, polyimide (PI) has been recognized as an engineering plastic with superior properties for over 40 years because of its high thermal stability (with glass transition temperatures in general being higher than 250 °C, and 5% decomposition temperatures over 400 °C), mechanical toughness, pliability, and outstanding electrical properties (*i.e.*, insulation and dielectric properties).[12,13] Hence, PI is widely applied in fields such as electronics and aerospace.

In this work, we synthesized and characterized a series of fluorinated polymaleimides that exhibit good thermal stability, controllable refractive index, and low optical loss in the optical communication wavelength of 1.55 mm.

Experimental

Materials. *N*-Phenylmaleimide (H-PMI), pentafluoroaniline, anhydrous sodium acetate, acetic anhydride, maleic anhydride (MA), 1,1,2,2-tetrachloroethane (TCE), chlorobenzene, and cyclohexanone were purchased from Sigma-Aldrich. 2,2-azobisisobutylnitrile (AIBN) was purchased from Acros. H-PMI and MA were purified through recrystallization. All other materials were analytical grade and used without further purification.

Synthesis of Pentafluorophenylmaleimide (F-PMI). The basic synthesis of the F-PMI monomer has been described in an earlier article.[14] In this study, a similar procedure has been employed, except for a few adjustments (Scheme 1). Pentafluoroaniline (1) (10 g, 54.64 mmol) was added to a reaction flask containing 5.8 g of maleic anhydride (2) (59.15 mmol) in 180 mL of methylene chloride. The solution was stirred for 30 minutes at room temperature, after which the solvent was removed by rotary evaporation. The thus-obtained crude *N*-pentafluorophenyl maleamic acid (3), 1.2 g of anhydrous

sodium acetate, and 12 g of acetic anhydride were heated for 30 min in a boiling water bath, yielding a dark brown-colored liquid that turned into a semisolid upon cooling to room temperature. The mixture was washed with dilute aqueous and extracted into ether. The ether layer was washed with saturated aqueous $NaHCO_3$ and dried over anhydrous $MgSO_4$. After removing the ether, the crude product was passed through a silica gel column using *n*-hexane/ethyl acetate (5:1 v/v) as the eluent. The product was dried in a vacuum oven for 24 h to remove residual solvent. F-PMI was further purified through recrystallization with ethanol. Yield = 83.7% (12.0 g), ^{1}H NMR (CDCl₃) δ 6.96 (s, 2H).
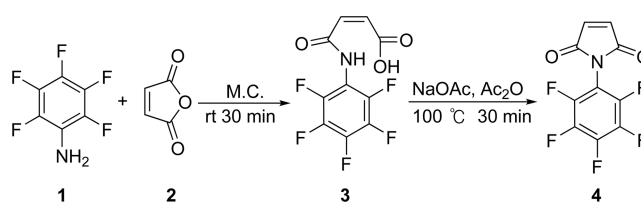
Polymerization of Poly(phenylmaleimide-co-pentafluorophenylmaleimide) (PPMI). The copolymers were prepared in a glass ampoule using TCE and AIBN as the thermal initiator. H-PMI and F-PMI were dissolved in TCE, and 1.0 wt % AIBN (*vs.* monomer) was added. The mixtures were subjected to four freeze–pump–thaw cycles to remove O_2 and sealed under vacuum. The sealed sample ampoules were immediately immersed in liquid N_2 to ensure that no pre-polymerization occurred. Polymerization was then initiated in an oil bath at 65 °C for 24 h. After polymerization was completed, the polymers were obtained as a pink powder by precipitation in methanol. Copolymer (PPMI): ^{1}H NMR (DMSO-*d₆*) δ 4.5 (b, sp³ hydrogen of the polymer main-chain), 7.4 (b, aromatic ring hydrogen of H-PMI).

Analysis. ^{1}H NMR spectral data were measured on a Varian Mercury-400 MHz NMR spectrometer in CDCl₃ and DMSO-*d₆*. Chemical shifts of ^{1}H NMR spectral data were referenced to tetramethylsilane (TMS) at 0 ppm. FT-IR spectra were recorded in KBr, using a Mb 100 (ABB Bomem) at a resolution of 4 cm^{-1}. Thermogravimetric analysis (TGA) of each of the polymers was performed on a TA Instrument SDT 2960 between 25-1000 °C at a heating rate of 20 °C/min. The refractive index, birefringence factor, and optical loss were measured using a prism coupler (Model 2010, Metricon). Optical absorption loss at 1.55 mm was performed by FT near-IR spectroscopy (Model N-400, Buchi).

Results and Discussion

F-PMI was synthesized in two steps by reaction of pentafluoroaniline (1) with maleic anhydride (2) and subsequent cyclodehydration of *N*-pentafluorophenyl maleamic acid (3) with acetic anhydride and sodium acetate (Scheme 1). The structure of the maleimide compound was confirmed by ^{1}H NMR. After reaction, the amine signal around 5.6 ppm had disappeared and only the sp² C–H bond around 6.96 ppm was observed in the NMR spectra.

H-PMI and F-PMI were copolymerized by radical polymerization using the thermal initiator AIBN (Scheme 2). Table 1 lists the feed ratio of the monomers, as well as the number average molecular weights (determined by GPC), and the quantitative analysis based on the NMR spectra. Compared to the F-PMI monomer, PPMI copolymers exhibited a peak at 6.96 ppm in the ^{1}H NMR spectrum, stemming from the sp² bonded hydrogen in the maleic acid

Scheme 1. Synthesis of pentafluorophenylmaleimide (F-PMI).

group of F-PMI. After polymerization, a broad signal at 4.5 ppm was observed, corresponding to the sp³ bonded hydrogen in polymer chain because of the replacement of the C=C bond with a C–C single bond. In the synthesized PPMI copolymers, the integration of the aromatic C–H at 7.3 ppm in H-PMI decreased as the feed ratio of F-PMI increased. The molecular structure of the PPMI copolymers was further characterized by FT-IR (Figure 1). The aromatic C–H stretch vibration of H-PMI at 3050 cm^{-1} decreased with an increasing F-PMI feed ratio, while the C–F stretching vibration at 1000 cm^{-1}, corresponding to the aromatic ring in F-PMI, increased in the PPMI copolymers. Thus, the ratio between H-PMI and F-PMI in the copolymers could be easily controlled by varying the feed ratio of the monomers. The number average molecular weight of the polymers decreased with an increasing F-PMI ratio because the reactivity of the monomers decreased as a result of the presence of the F-PMI pentafluorophenyl group.

For optical and electronic applications, polymeric materials should have sufficient thermal stability to withstand prolonged periods of temperature variations during device fabri-
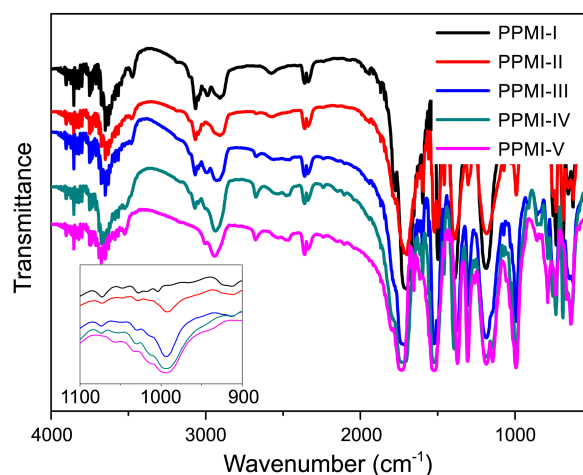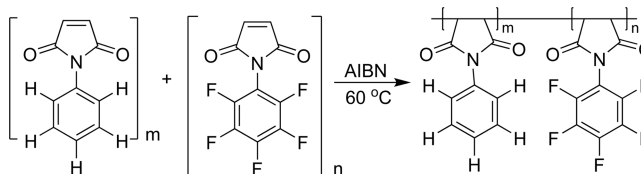

Figure 1. Infrared spectrum of PPMI. The inset shows the aromatic C–F stretching vibration at 1000 cm^{-1}.
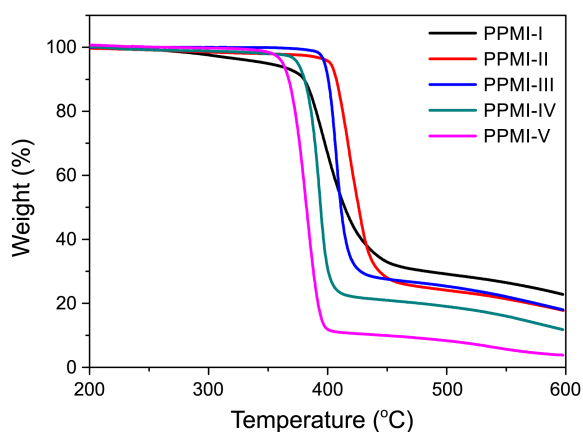

Scheme 2. Synthesis of PPMI copolymers *via* radical polymerization.

Table 1. The feed ratio of monomer, number average molecular weight, and quantitative NMR analysis of PPMI copolymers

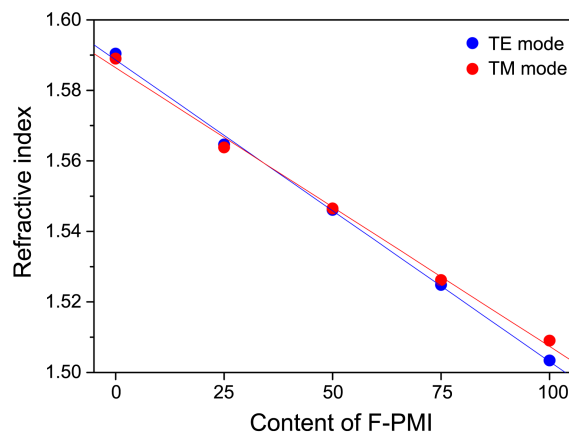|	Feed ratio (mol %)		M_n^a	PDI[b]	[1]H Integration at 4.5	[1]H Integration at 7.3	Mole fraction of H-PMI in copolymer
	H-PMI	F-PMI					
PPMI-I	100	0	38,300	2.3	4	11.76	1
PPMI-II	75	25	27,300	2.6	4	8.92	0.756
PPMI-III	50	50	22,700	2.8	4	7.37	0.625
PPMI-IV	25	75	15,600	1.7	4	3.13	0.265
PPMI-V	0	100	12,100	1.5	4	0	0

[a]M_n: Number average molecular weights determined by GPC. [b]PDI: Polydispersity index.

Figure 2. TGA of the PPMI copolymers series.

Figure 3. The refractive index of the PPMI copolymer series in TE (red) and TM (blue) mode.

Table 2. Optical properties of PPMI copolymers at a wavelength 632.8 nm

	n_{TE}	n_{TM}	Birefringence	Optical loss (dB/cm)
PPMI-I	1.5950	1.5932	0.0018	2.64
PPMI-II	1.5762	1.5757	0.0005	1.61
PPMI-III	1.5540	1.546	0.0006	1.58
PPMI-IV	1.5294	1.5312	0.0018	1.28
PPMI-V	1.4969	1.4993	0.0024	-

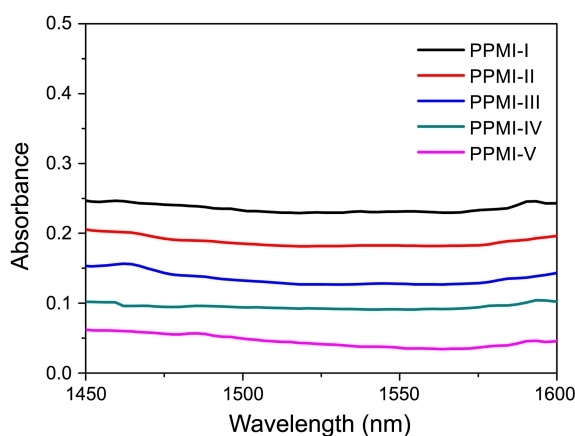**Figure 4.** Absorbance of the PPMI copolymer series at 1.55 mm wavelength.

cation and operation. We confirmed the superior temperature stability of PPMI copolymers using thermogravimetric analysis. As shown in Figure 2, all PPMI copolymers display high thermal stability with a T_d over 380 °C. The decomposition temperatures are slightly decreased as F-PMI content increased in PPMI copolymer. It's similar to other results which explain why fluorinated analogues have decomposition temperatures lower than those of the hydrocarbon parent polymers.[15,16]

Control over the refractive index in transverse electric (TE) and transverse magnetic (TM) modes is of key importance for the functioning of optical waveguide materials. We could easily vary the refractive index of the PPMI copolymers through variation of the fluorine content, which in turn was determined by the F-PMI ratio. PPMI films were prepared by spin-coating at 2000 rpm for 30 s and their refractive indices were determined by the prism coupling method at 632.8 nm (Figure 3). The refractive index of the copolymers could readily be tuned from 1.4969 to 1.5950 in the TE mode and from 1.4993 to 1.5932 in the TM mode. It was found that an increase in the ratio of the pentafluorophenyl group led to a linear decrease in the refractive index of the PPMI copolymers for both the TE and TM mode, owing to the increase in fluorine content.[15] Table 2 shows the birefringence of PPMI copolymers as a function of the monomer ratio. Also the birefringence of the PPMI could therefore be controlled by the monomer feed ratio. The low birefringence is necessary to reduce factors such as polarization-dependent loss in optical waveguide devices.[17]

The absorption spectrum of the PPMI series was measured by FT near-IR spectroscopy at the optical communication wavelength of 1.55 μm (Figure 4). All PPMI copolymers

exhibited low absorbance in the UV-visible region, showing a decrease in the absorption value with an increasing F-PMI ratio. We also measured the optical loss of the prepared PPMI copolymer series. As shown in Table 2, the optical loss decreased with an increasing F-PMI ratio, owing to the low polarizability of the C−F bond.[18] From these results, we confirmed that PPMI copolymers can successfully be applied as optical waveguides.

Conclusion

In this study, we synthesized a series of fluorinated polymaleimides from H-PMI and F-PMI monomers, to combine high thermal stability with low optical loss. All PPMI copolymers displayed high thermal stability with a T_d over 380 °C. The refractive index of the copolymers could readily be tuned from 1.4969 to 1.5950 in the TE mode and from 1.4993 to 1.5932 in the TM mode. The optical loss of the copolymer series decreased with increasing F-PMI content at the optical wavelength of 632.8 nm, while all PPMI copolymers displayed low absorption loss at 1.55 mm wavelength. We expect our PPMI copolymer series to be useful in optically responsive materials with controllable refractive index.

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