

SHORT COMMUNICATION

Fluorinated Poly(phthalazinone ether)s with Tunable Refractive Index: Synthesis, Characterization and Optical Properties

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Integrated optics is expected to develop optical communication and optical sensing due to its high bandwidth and high resistibility of electromagnetic interference.¹ Extensive studies have been conducted on the development of new materials, which exhibited suitable properties for application in optical telecom and datacom technology.² An optical waveguide generally consists of a waveguide core, in which the signal propagates, and a cladding, which surrounds the core and detains the optical signal inside the waveguide core. And it is essential for the core material to have a higher refractive index than the cladding in order to confine the light. Therefore, materials with a controllable refractive index are required for successful design and fabrication of photonic devices. Additionally, good film-forming properties, high thermal stability, and low optical losses at the telecommunication wavelengths of 1.3 and 1.55 μm are also required for materials used in optical applications.³ Among the candidates, polymers are more attractive for optical waveguide applications due to their ease in processing, controllability of optical properties, and their cost-effective technology. Thus a significant amount of research efforts have been performed on polymers for use as optical waveguide applications.⁴ However, most hydrocarbon-based polymers show a large transmission loss in the visible and near-IR region due to the vibrational overtone absorption of the C-H, O-H, and N-H bonds. A common method to minimize this kind of loss is to replace the C-H bonds by C-X (halogen) bonds in the result of their absorption overtones to longer wavelengths, thereby reducing the intrinsic optical loss in 1310 nm and 1550 nm. Work carried out in a number of laboratories has demonstrated that halogenations, particularly fluorination, could offer interesting opportunities for the alteration of properties such as refractive index, hydrophobicity and thermal stability. Therefore, a wide range of fluorinated polymers have been developed and demonstrated their promising waveguiding properties.⁵ Among them, fluorinated poly(arylene ethers) have exhibited the best integrated properties.⁶ However, the conventional synthesis of those polymers, which is usually conducted by a nucleophilic aromatic substitution ($\text{S}_{\text{N}}\text{Ar}$) polycondensation between aromatic dihalide and diphenol compounds in *N,N'*-dimethylacetamide (DMAc) with an excess of anhydrous potassium carbonate at high temperatures (*e.g.*, 160 °C), prevalently leads to side reactions such as branching or cross-linking.⁷ Consequently, continuous efforts on the synthesis of the new fluorinated polymers with easy processability are still worth making for optical applications.

It is supposed that poly(phthalazinone ether)s will be particularly suitable to be used as potential polymeric optical materials after being partially fluorinated due to their relatively modest synthetic condition, extraordinarily high T_g (265–305 °C), excellent thermal stability and good thin film processability.^{8–10} Herein, we reported the synthesis of novel

fluorinated poly(phthalazinone ether)s prepared by the modified polycondensation reaction. The structure and optical properties of the resulting polymers were also investigated. By adjusting the feed ratio of the reactants, the refractive indices could be well controlled.

EXPERIMENTAL

Polymer Synthesis

A series of novel fluorinated poly(phthalazinone ether)s (FPPEs) were synthesized as illustrated in Scheme 1.

A typical preparation of these polymers (FPPE-2) was illustrated as follows. To a solution of 4,4'-(hexafluoroisopropylidene)diphenol (6F-BPA, 5 mmol, Sigma-Aldrich), 4-(4'-hydroxyphenyl)phthalazin-1(2*H*)-one (DHPZ, 15 mmol, Dalian Polymer New Material Co. Ltd.) and decafluorobiphenyl (DFBP, 20 mmol, Sigma-Aldrich) in 10 mL of anhydrous *N,N'*-dimethylacetamide (DMAc) was added potassium fluoride (KF, 16 mmol) and calcium hydride (CaH_2 , 40 mmol). The mixture was stirred at 90 °C under nitrogen for 4 h. After filtration, the viscous solution was slowly poured into sufficient ethanol with the presence of hydrochloric acid in drops. The resulting polymer product was collected by filtration, washed thoroughly with pure water and methanol, and dried at 80 °C for 24 h under vacuum (93% yield). ¹H-NMR (400 MHz, CDCl_3 , ppm) δ : 7.06 (m, 3H), 7.22–7.92 (m, 13H), 8.63 (s, 1H). ¹⁹F-NMR (376 MHz, CDCl_3 , ppm) δ : –64.06 (s, 2F), –136.76 (m, 1F), –137.47 (m, 5F), –143.32 (m, 2F), –152.44 (m, 3F).

Film Preparation and Optical Properties Measurements

The resulting polymers were dissolved in cyclohexanone at a concentration of 20% (w/v). Then the solution was filtered through a 0.45 μm Teflon microfilter and spin-coated on a Si/SiO₂ substrate. In order to guarantee the quality of the spin-coated films, the whole spin-coating procedure was carried out in a 1000 class ultraclean room. The resulting films were dried at 60 °C (30 min) and 120 °C (4 h) to remove the residual solvent under vacuum. The optical properties of the polymer films, such as the refractive index, thermo-optic coefficient and optical loss were measured with a Sairon SPA-4000 prism coupler.

RESULTS AND DISCUSSION

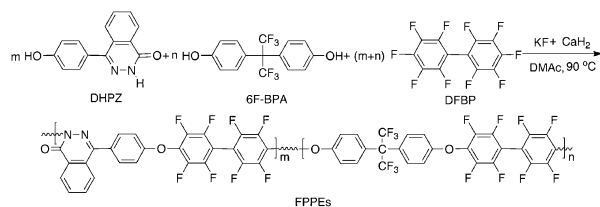
In this reaction, potassium fluoride acted as a catalyst to convert the phenol group to the phenolate. Additionally, as reported previously,¹¹ it also acted as a base to combine with HF to form a KHF_2 complex and precipitate it out of the solution, thereby promoting the polymerization

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Scheme 1. Synthetic route of FPPEs.

Table I. Thermal and Optical Properties of FPPEs

Polymers	Feed Ratio ^a	T_g^b (°C)	dn/dT^c ($\times 10^{-4}/^\circ\text{C}$)		Optical Loss ^d (dB/cm)
			TE	TM	
FPPE-1	0/1	253	-1.24	-1.16	0.210
FPPE-2	1/3	284	-1.10	-0.85	0.146
FPPE-3	1/1	267	-0.96	-0.74	0.169
FPPE-4	3/1	292	— ^e	— ^e	0.270

^aThe feed mole ratio of 6F-BPA/DHPZ. ^bGlass transition temperature measured by DSC with a heating rate of 10 °C/min in nitrogen. ^cThermo-optic (T-O) coefficient (dn/dT) of the TE mode at 1310 nm. ^dMeasured on slab waveguide samples using the high-index liquid immersion technique at 1310 nm. ^eNot tested.

reaction. Meanwhile, the neutralizing effect could also be achieved by the use of CaH_2 . No peak attributed to branch structure existed in the ^{19}F -NMR spectra suggested that a good control of the linear structure was obtained for FPPEs under this condition.

The resulting polymers exhibited excellent solubility in polar organic solvents (*e.g.*, THF, CHCl_3 , cyclohexanone), which makes it easier for film preparation and device fabrication. Furthermore, compared to those highly fluorinated poly(arylene ether)s,⁵ FPPEs showed higher thermal stability, and the glass transition temperatures (T_g s) ranged from 253 to 292 °C (Table I).

Fine-tuning of materials' refractive index is exceedingly important for its optical waveguide applications. The refractive indices of the FPPEs were investigated by using the prism-coupling method on thin films. By adjusting the feed ratio of DHPZ/6F-BPA, thereby changing the fluorine content, the refractive indices of TE and TM modes decreased linearly from 1.573 to 1.498 and from 1.548 to 1.484, respectively (see Figure 1). The linear dependency of their refractive indices on the fluorine content allowed the control of the refractive indices of the FPPEs. It should be noted that the birefringence ($\Delta n = n_{\text{TE}} - n_{\text{TM}}$) of the FPPEs was a little higher in this work (~ 0.02). Some further studies on minimizing the birefringence to an acceptable value are currently under way.

The optical losses of FPPEs were evaluated from the slab waveguide loss using high index liquid immersion method,¹² and the results were summarized in Table I. These relatively low optical losses of the polymers could be ascribed to the replacement of C-H units by C-F units which could shift the associated vibrational overtone to longer wavelengths, thereby increasing the optical transparency in the near-infrared communication region.

Besides refractive index and optical loss, thermo-optic (T-O) coefficient (dn/dT) also plays a vital role in indicating the optical properties of the polymer. A large T-O coefficient corresponds to a small temperature

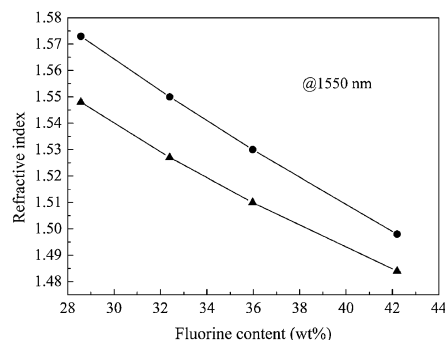


Figure 1. Relationship between the refractive index and fluorine content (wt%) of FPPEs. (●) at TE mode. (▲) at TM mode.

change and thus a small power input for causing the necessary change in the refractive index of polymer waveguides. The dn/dT values of FPPEs, which are one order of magnitude larger than those of inorganic glasses,⁵ are especially useful for devices in which thermal jump actuation is utilized for switching optical communication signals from one optical circuit to another.³

In summary, the obtained fluorinated poly(phthalazinone ether)s, which were prepared by the modified synthetic procedure, exhibited excellent solubility, high thermal stability and good optical properties. By adjusting the feed ratio of the reactants, the refractive indices could be well controlled. These results indicate that the application of FPPEs in the field of optical waveguide appears feasible and promising.

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REFERENCES

- S. K. Sharma, S. C. K. Misra, and K. N. Tripathi, *Optik*, **114**, 106 (2003).
- L. Eldada and L. W. Shacklette, *IEEE J. Sel. Top. Quant. Electron.*, **6**, 54 (2000).
- H. R. Allcock, J. D. Bender, Y. Chang, M. McKenzie, and M. M. Fone, *Chem. Mater.*, **15**, 473 (2003).
- K. Han, K. You, W. H. Jang, and T. H. Rhee, *Macromol. Chem. Phys.*, **201**, 747 (2000).
- H. Ma, A. K. Y. Jen, and L. R. Dalton, *Adv. Mater.*, **14**, 1339 (2002).
- J. F. Ding, Qi Y, M. Day, J. Jiang, and C. L. Callender, *Macromol. Chem. Phys.*, **206**, 2396 (2005).
- J. F. Ding, X. Du, M. Day, J. Jiang, C. L. Callender, and J. Stupak, *Macromolecules*, **40**, 3145 (2007).
- L. Z. Chen, X. G. Jian, and X. L. Zhu, *Polym. J.*, **31**, 393 (1999).
- S. Xiao, J. Wang, K. Jin, X. Jian, and Q. Peng, *Polymer*, **44**, 7369 (2003).
- P. Liu, Q. Liang, C. Liu, X. Jian, D. Hong, and Y. Li, *Polym. J.*, **38**, 477 (2006).
- Y. Qi, J. F. Ding, M. Day, J. Jiang, and C. L. Callender, *Chem. Mater.*, **17**, 676 (2005).
- C. C. Teng, *Appl. Opt.*, **32**, 1051 (1993).