

Hyperbranched fluorinated polyimides with facile tunable refractive index for optical waveguide application

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A series of halogenated terminal hyperbranched polyimides (HBPI)s with facile tunable refractive index had been designed and prepared as optical waveguide materials. These polymers were endowed with the multifarious and controllable chemical structures as well as a facility synthesized method. Due to the high polarizability of the C-Cl bonds in the terminal groups, the refractive indices (RIs) were accurately controlled by adjusting C-Cl bonds content without additional optical loss. Finally, a kind of waveguide devices fabricated by reactive ion etching (RIE) from the polymer exhibited good optical propagation at wavelength of 1.55 μm .

1. Introduction

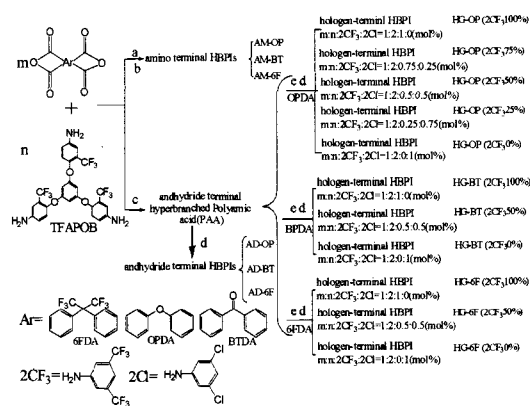
Polymer optical waveguides have attracted considerable attentions for their possible application as light transmission components in optical communication systems [1-3]. For advanced integrated optical waveguide applications, the polymer optical materials should have excellent properties in terms of low optical loss, low birefringence[4,5], high T_g ect.. Towards meeting all these materials' requirements, various types of waveguide polymers have been developed. Here, a series of HBPIs with different halogenated terminal groups were synthesized as optical waveguide materials, the physical and optical properties of these HBPIs were also exhibited.

2. Experimental section

2.1 Polymer Synthesis

2.1.1. Synthesis of anhydride terminal HBPIs

The general polymerization procedure was outlined in scheme 1. A typical procedure for the polyaddition of TFAPOB with OPDA was as follows. To a solution of 2 mmol (0.62 g) dianhydred (OPDA) in dried DMAc (10 mL) in a 50 mL flask, 1 mmol (0.604 g) of TFAPOB dissolved in 5 mL of DMAc was added dropwise through a syringe over 1 h. The mixture was stirred at 40 °C for about 24 h to afford anhydride terminal poly (amic acid) solution. The poly (amic acid) was subsequently converted to polyimide through chemical imidization process. Chemical imidization was carried out via the addition of 1 g of triethylamine and 3 g of acetic anhydride into the poly (amic acid) solution at 40 °C for 8 h. The resulting homogeneous polyimide solution was poured into ethanol to give a white precipitate, which was collected by filtration, washed thoroughly with ethanol and dried under vacuum at 80 °C for 24 h. The obtained polymer was signed as AD-OP. AD-BT and AD-6F can be prepared using the same procedure.



Scheme 1. Synthesis of HBPIs.

2.1.2. Synthesis of halogen terminal HBPI

The 3,5-ditrifluoromethylaniline (x mmol) ($x=0, 0.5, 1$) and 3,5-dichloroaniline ($1-x$) were added into the same amount of OP-HBPI poly(amic acid) precursors prepared by the same procedures above. The reaction mixtures were stirred at 40 °C for 8 h. Then, a mixture of triethylamine (1 g) and acetic anhydride (3 g) was added, and was stirred at 40 °C for another 8 h. After cooling to room temperature, the mixture was precipitated from ethanol (200 mL). The polymers were collected by filtration and dried under vacuum at 80 °C for 24 h. The obtained polymers were signed as HG-OP (2CF₃100%) ($x=1$), HG-OP (2CF₃50%) ($x=0.5$), HG-OP (2CF₃0%) ($x=0$). HG-BT and HG-6F series were also prepared using the same procedure. The polymer of $x=0.25$ and 0.75 were prepared in the series of HG-OP used for research of RI in detail. The polymerization procedures were also outlined in scheme 1.

2.2. Waveguide fabrication

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

3. Results and discussion

In the case of halogen terminal polymers, the ¹H NMR could not describe the structure of the terminal halogen groups in detail, and the different halogen terminal structures were confirmed by ¹⁹F NMR (Fig.1). The peaks at -61.5 ppm and -63.7 ppm were attributed to CF₃ from 6FDA and triamine respectively, and the peak around -62 ppm was assigned to the CF₃ associated with terminal monomer 3,5-ditrifluoromethylaniline. No obvious signal related to the 3,5-dichloroaniline terminal polyimides was detected. The results indicated that control of fluorine content of the HBPI could be easily achieved by varying the feed ratio of terminal monomers.

All the polymers exhibited rather good thermal properties with 5% weight-loss above 500 °C. DSC results revealed the glass-transition temperature (T_g) of the HBPIs in the range 200-243 °C. T_g of the

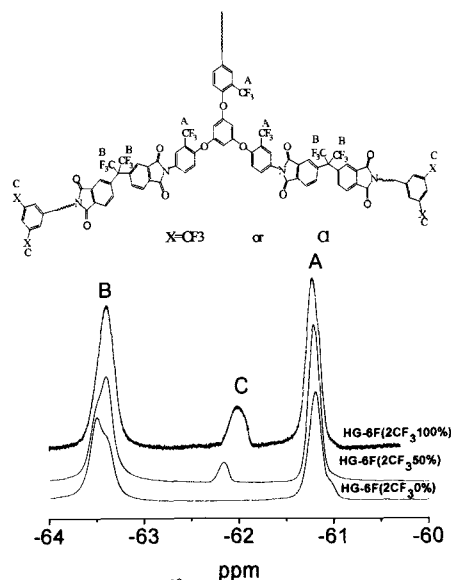


Fig. 1. ¹⁹F NMR spectra of the

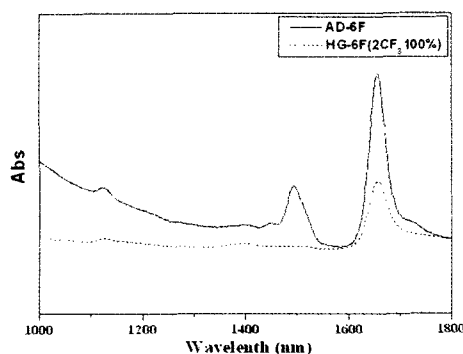


Fig.2 Near-IR spectra of AD-6F (solid line) and HG-6F (2CF₃ 100%) (dotted line).

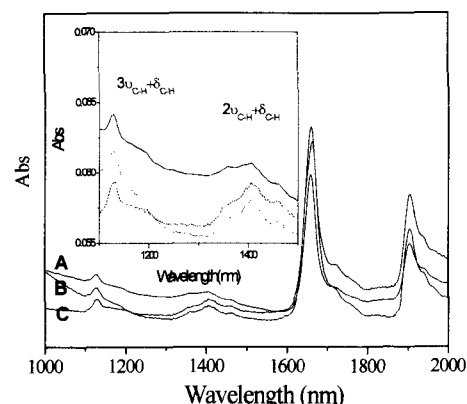


Fig. 3. Near-IR spectra of HG-OP (A: HG-OP (2CF₃100%); B: HG-OP (2CF₃50%); C: HG-OP (2CF₃0%).

halogen terminal HBPIs were decrease because of the chemical substitution. This can be explained by the decrease in the end-group polarity of the anhydride terminal polyimides.

In this paper, the absorptions of halogen terminal HBPIs were researched by near-IR spectra. The end-capped polymers showed lower attenuation loss than the uncapped ones at optical communication wavelength due to the presence of the trifluoromethyl and chloro groups (Fig.2). In the case of halogen terminal polymers (Fig. 3), the absorption peaks were normalized by dividing with their film thickness. The presence of the halogen-carbon bonds in the HBPI induced the shift of the hydrogen-carbon overtone absorption to longer wavelength and reduced the intrinsic loss at the telecommunication wavelengths. Both chloro- and trifluoromethyl terminal polymers exhibited the similar attenuation at telecommunication wavelengths due to the similar low second harmonic (overtone) vibrational absorption[6-9], which can avoid further optical loss bring by introducing C-H.

The refractive indices of the halogen terminal HBPIs were studied by ellipsometer. The values were in the range of 1.5160-1.5309 for HG-6F series, 1.5807-1.6109 for HG-OP series and 1.5863-1.5944 for HG-BT series, respectively. It is well known that the polarizability of the carbon-chlorine (C-Cl) bond is larger than that of C-F bond. HG-6F series showed relatively lower RIs because of their higher fluorine content. In fact, a good linear relationship, between the refractive index and trifluoromethyl content was observed as shown in Fig. 4. Taking HG-OP series as the example, when the feed ratio of (3,5-trifluoromethyl)aniline was increased from 0 to 100%, the refractive index increased from 1.5807 to 1.6109. This linear relationship represented an opportunity for the fine-tuning of the RI by easy changing the feed ratio of terminal monomers. Compared to the linear copolymerization method, the modification of the end groups of hyperbranched polymer by different halogen monomers was a straightforward and efficacious route for potential waveguide materials. The birefringences of HBPIs were found as low as 0.003 which were lower than those of LPIs [10]. The low birefringence was contributed to the geometry of the repeat units. In the chemical structures of HBPIs, the triamine, i.e., the 'core' molecule was expected to define the configuration of the repeat units primarily. The single-crystal X-ray analysis revealed that the triamines in the repeat units were non-planar and asymmetric in geometry (See Fig. 5). Therefore, the triamine monomers in the polymers could prevent the orientation of polymer chains effectively, and reduced the birefringence obviously. Based on all the results, HBPIs from the new triamine monomer should be a promising candidate for optical waveguide materials.

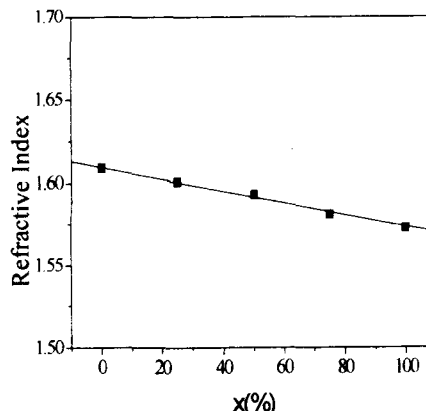


Fig. 4. Relationship between the RIs and the content of (3,5-trifluoromethyl)aniline (x= molar ratio of (3,5-trifluoromethyl)aniline to the total terminal groups).

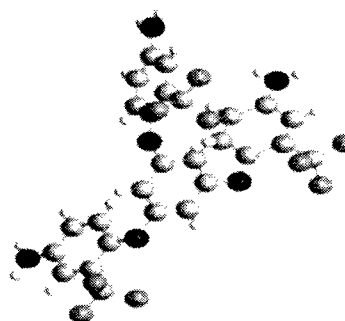


Fig.5. X-Ray structure of the triamine monomer.

As a result, a simple waveguide device was fabricated using these HBPIs by reactive ion etching (RIE) technique. Fig.6 showed an atomic force microscope (AFM) image of the polymer waveguide. In the 3D micrograph of the pattern, smooth surfaces for both the top and sidewall were obtained. From the results of AFM image, it was observed that the films were about 1 μm thick and the surface roughness of the waveguide beam was less than 5 nm. The near-field mode pattern at the out channels (Fig. 7) was observed with an infrared vidicon after being magnified by an objective lens. These results had demonstrated that the fluorinated HBPIs were a promising candidate for optical waveguide with low optical loss.

4. Conclusions

A series of halogen terminal hyperbranched polyimide were successfully prepared. All the halogen terminal HBPIs had excellent physical properties, including the high glass transition temperatures, good thermal stabilities, easy of film processing ect.. Furthermore, halogenated HBPIs exhibited the excellent optical properties. It was validated that the high halogen content could increase the film transparency, and the hyperbranched isotropic structures could lower the birefringences. By modifying the large numbers of end active groups with fluorinated and chlorinated monomers, the polymers would have the accurately tunable refractive indices and the low optical loss at the same time. Consequently, the waveguide devices were fabricated by RIE from these materials and exhibited good optical propagation at 1.55 μm .

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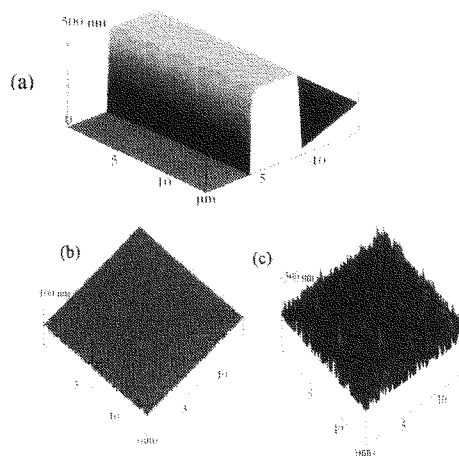


Fig. 6. AFM image of polyimide: (a) AFM 3D micrograph of the pattern, (b) Surface roughness of the waveguide beam measured by AFM, (c) Surface roughness of the silica layer of the substrate measured by AFM.

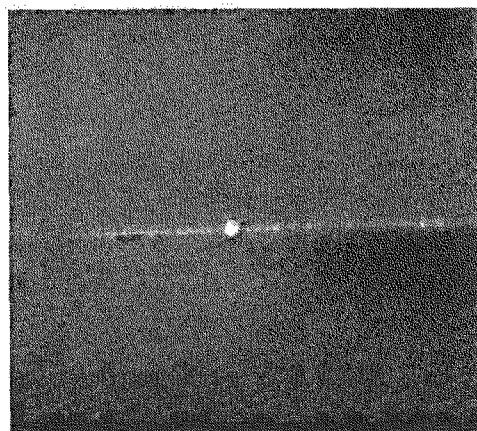


Fig. 7. AFM image of polyimide: (a) AFM 3D micrograph of the pattern, (b) Surface roughness of the waveguide beam measured by AFM, (c) Surface roughness of the silica layer of the substrate measured by AFM.