Synthesis of fluorine-containing terminated with crosslinkable moieties

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Introduction

Considerable attention has been devoted to the preparation of fluorine-containing polymers because of their unique properties and high temperature performance.[1] Fluorinated poly(aryl ethers) developed for low dielectric constant materials are proved to be good candidate for the optical waveguide devices due to their high thermal stability, low moisture absorption, and low optical absorption at the near-infrared region.[2] To improve chemical resistance and sharp-cleaving properties of polymeric films, crosslinkable groups at the chain ends have been introduced.[3]

In this study, to satisfy the demands of fabrication processing and operation conditions, we synthesized a kind of fluorinated poly(aryl ether) with a crosslinkable phenyl ethynyl moiety. A cross-linked polymer had high glass transition temperature and good chemical resistance. The thin film of cross-linked polymer exhibited low light absorption at the telecommunication wavelength.

Experimental

Preparation of Polymer Film. The sample for near-infrared measurement was prepared by spin-coating the polymer solution onto quartz wafer (NMP was used as a solvent). The coated film was dried at 130 °C for 30min, and then annealed at 350 °C for 2h.

Synthesis of 4-phenyl ethynyl phenol (PEP). A yellow solid was obtained according to the literature.[4]

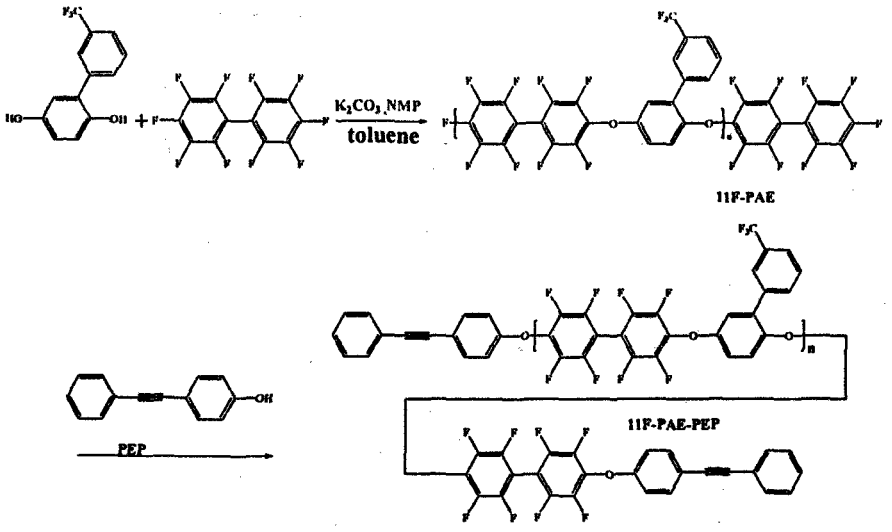
Ms: 194[M$^+$]. ^{1}H NMR($CDCl_3$): δ7.50(d, 2H); 7.43(d, 2H); 7.37(m, 3H), 6.81(d, 2H), 4.96(s, 1H).

Synthesis of 11F-PAE. A typical polymerization procedure was as follows (**Scheme 1**): (3-trifluoromethyl)phenylhydroquinone(2.54g, 0.01mol), Decafluorobiphenyl(3.67g,0.011mol), K_2CO_3(4.14g,0.03mol), NMP(40ml) and toluene(65ml) were put in a reaction flask equipped with a nitrogen inlet, magnetic stirrer, and Dean-Stark trap. The polymerization was allowed to react at 130°C for 4h. The mixture was poured into 200ml water/methanol (1:1 solution). The precipitated polymer was filtered and washed with deionized water. The white solid was dried under vacuum (80°C) for 24h. Molecular weight: Mn= 9200 with a polydispersity of 1.34.

Synthesis of 11F-PAE-PEP. A typical reaction procedure was as follows: The reaction equipment was the similar to that of 11F-PAE.11F-PAE(3.67g), PEP (0.31g), NMP(20ml), K_2CO_3(0.34g) and toluene(60ml) were added to the flask. The mixture was stirred and reacted at 130°C for 4h. The reaction mixture was cooled and precipitated into 200ml of deionized water /methanol (1:1 solution). The precipitated polymer was filtered and washed with deionized water. The polymer was vacuum dried at 80°C.

FTIR (KBr): [illegible] (-O-), 1129 (-CF_3), 1072 (Ar-F).

^{1}H NMR (CDCl3): δ7.54-7.34(small peaks, end groups), 7.83(s,1H), 7.75(d,1H),7.63(d,1H), 7.57(t,1H), 7.16(s,1H), 7.04(d,1H), 7.69(d,1H)



Scheme 1. Synthesis of 11F-PAE-PEP.

Results and Discussion

The molecular weight of polymer could be controlled by adjusting feed radio of monomers. The FTIR and ^{1}H NMR spectra were agreed with the supposed structure. In the ^{1}H NMR spectrum of 11F-PAE-PEP, the absorption peaks of phenyl ethynyl moiety could be observed besides the other characteristic peaks.

To study the thermal behavior and the crosslinking of the polymer, DSC was performed. Intense exothermic peak due to the crosslinking reaction of phenyl ethynyl moiety was observed.

The crosslinking reaction started at around 340°C, and showed maximum at 420°C. No further exothermic peak was observed when the polymer was rerun.

After curing the polymer, the Tg of 11F-PAE-PEP increased from 126°C to173°C. The thermal stability of cross-linked 11F-PAE-PEP was investigated by TGA in air. The temperature at which a 5% weight loss was observed was 522 °C.

11F-PAE-PEP could dissolve in DMF, DMAC, NMP and chloroform before curing. After curing, the polymer film couldn't dissolve in above solvents.

A near-infrared spectrum was used to evaluate the absorption at the wavelength of optical communication, 1.0-1.7μm (**Figure 1**). Except for a small absorption peak, which was due to moisture (υOH(H_2O)) or the combination of the second harmonics of the stretching vibration and the deformation vibration of the C-H bond (2$u^{\varnothing}$CH+$\delta^{\varnothing}$CH, 1.38μm), the cross-linkable highly fluorine-containing 11F-PAE-PEP had no substantial absorption peaks over the entire wavelength of optical communication, especially at the telecommunication wavelength of 1.3 and 1.55μm.

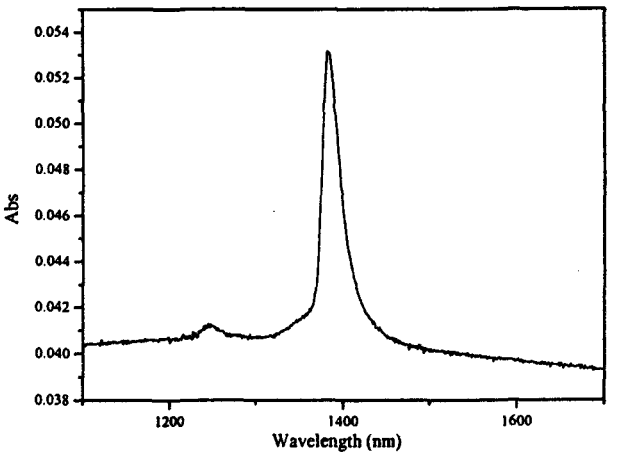


Figure 1. Light absorption of 11F-PAE-PEP in near-infrared region.

Conclusions

A highly fluorinated cross-linkable poly(aryl ether) was synthesized. The cross-linked polymer offered highly thermal stability, higher glass transition temperature, good chemical resistance and low optical absorption at the near-infrared region.

Acknowledgement. We gratefully acknowledge financial support from the High Technology Research and Development Program NO.863-715-0010.

References

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