Synthesis of fluorine-containing poly(aryl ether ketone) terminated with phenyl ethynyl group

Xiaoye Ma, Dong Wang , Shaowei Guan, Guibin Wang, Zhenhua Jiang
Department of Chemistry, Jilin University, Changchun 130012, China

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 ether ketone)s 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 solvent resistance 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 ketone) with a crosslinkable phenyl ethynyl group. A cross-linked polymer had high glass transition temperature and good chemical resistance.

Experimental

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

Synthesis of 3F-PEEK.

A typical polymerization procedure was as follows (**Scheme 1**): (3-trifluoromethyl) phenyl hydroquinone (7.62g, 0.03mol), 4,4′-difluorobenzophenone (7.848g,0.036mol), K_2CO_3(4.347g, 0.0315mol), DMAc(62ml) and toluene (35ml) were put in a reaction flask equipped with a nitrogen inlet, magnetic stirrer, and Dean-Stark trap and a condenser. The reaction mixture was allowed to reflux for 2 h. The toluene was removed by distillation. The system was heated to 160 °C. The polymerization was allowed to react at 160°C for 6h. The mixture was poured into1000ml acidic water. The precipitated polymer was filtered and washed with methanol and deionized water. The white solid was dried under vacuum (80°C) for 24h. Molecular weight: *Mn* 6500with a polydispersity of 1.48.

Synthesis of 3F-PEEK-PEP.

A typical reaction procedure was as follows: The reaction equipment was the similar to of 3F-PEEK. 3F-PEEK(7g), PEP(1.358g), DMAc (30ml), K_2CO_3 (0.5g) and benzene (25ml) were added to the flask. The reaction mixture was allowed to reflux for 1.5 h. The benzene was removed by distillation. The system was heated to 120 °C and reacted for 6h. The reaction mixture was poured into 200ml acidic water. The precipitated polymer was filtered and washed with methanol and deionized water. The white solid was dried under vacuum (80°C) for 24h. Molecular weight: M_n 5500with a polydispersity of 1.49.^{13}C-NMR ($CDCl_3$): 88.6, 89.4 (ethynyl).

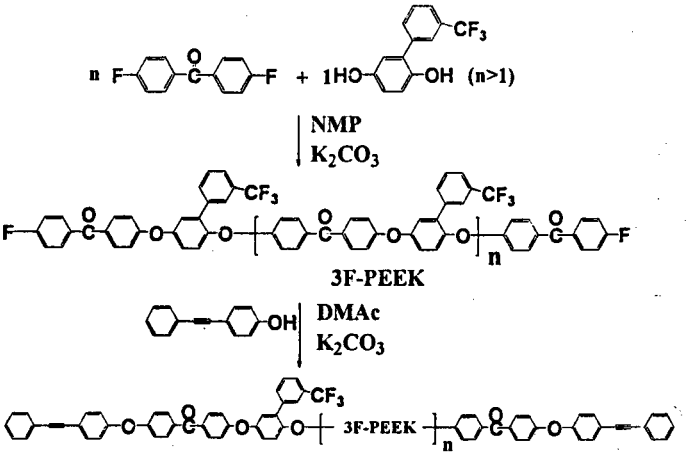
Results and Discussion

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.

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 group was observed. The crosslinking reaction started at around 350°C, and showed maximum at 441°C. No further exothermic peak was observed when the polymer was rerun. After curing the polymer, the Tg of 3F-PEEK-PEP increased from 116°C to 163°C. The thermal stability of cross-linked

3F-PEEK-PEP was investigated by TGA in nitrogen atmosphere. The temperature at 5% weight loss was observed was 526 °C.

3F-PEEK-PEP could dissolve in DMF, DMAc, NMP and chloroform before curing. After curing, the polymer film couldn't dissolve in above solvents.



Scheme 1. Synthesis of 3F-PEEK-PEP

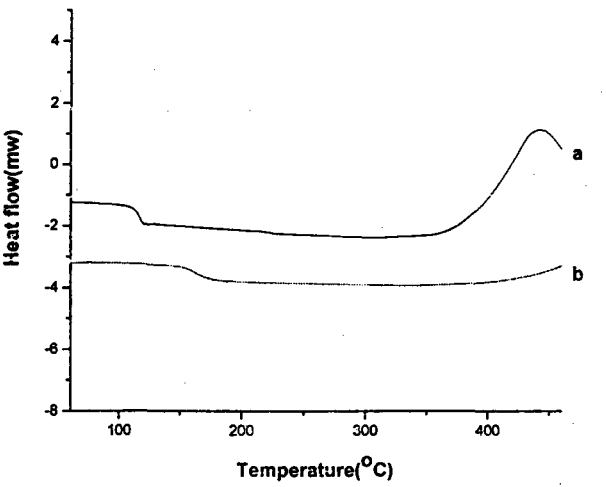


Figure 1. DSC trace of the 3F-PEEK-PEP (a) first scan (b) second scan

Conclusion

A fluorinated cross-linkable poly(aryl ether ketone) was synthesized. The cross-linked polymer offered highly thermal stability, higher glass transition temperature, good chemical resistance and solvent resistance.

References

(1) Cassidy, P.E.; Aminabhavi, T.M. *J.Macromol. polym. Sci. Rev. Macromol. Chem. phys.* 1989, C29, 365.

(2) Goodwin, A.A.; Mercer,F.W.; Mckenzie, M.T. *Macromolecules* 1997, 30, 2767.

(3) Kim, J.P.; Lee, W.Y.; Lee, J.S. et al. Macromolecules 2001,34,7817.

(4) Lee, H.J.; Lee, E.M.; Lee. M.H. et al. *J. Polym. Sci.: Part A:Polym.Chem.* 1998,36, 2881-2887.

(5) Baijun Liu; Guibin Wang; Wei Hu, et. al. *Journal of Polymer Science: Part A: Polymer Chemistry*, 2002, 40, 3392–339