

The Synthesis and Characterization of Novel Sulphonated PEEK Containing (3-Trifluoro methyl)phenyl Side Group.

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Introduction:

High performance polymers, such as poly(aryl ether ketone)s, poly(aryl ether sulfone)s, are well known for their excellent thermal properties, mechanical properties, dielectric properties, and oxidative resistance. These polymers have been found many applications in aerospace, coating and insulating materials. Chemical modification of polymers can be employed to tailor the properties of many materials. Recently, the sulphonation of these polymers as the candidate materials for proton exchange membrane attracted more and more attentions. Sulphonation of poly(ether ether ketone), poly(ether sulfone), poly(phenylene sulfide), and poly(benzimidazole) are examples that have been studied.^{[1]-[6]} In the past studies, two main approaches were adopted to attach sulfonic acid group in polymer. One is the sulfonation of polymers with some sulfonation agents, such as concentrated sulfuric acid, chlorosulfonic acid, etc, called *post-sulfonation* route, and the other is to first synthesize a sulfonic acid containing monomer and then polymerize it. Compared with the first approach, in the latter approach, the sulphonation degree can be easily controlled and the polymers have enhanced stability and modestly higher acidity due to the sulfonic acid group attached on deactivated phenyl ring.^[7] So in our studies, we adopted the second approach. The nucleophilic aromatic substitution polymerization of (3-trifluoromethyl)phenyl hydroquinone with sodium 5,5'-carbonylbis(2-fluorobenzene-sulfonate) affords novel sulfonated PEEK containing (3-trifluoro methyl)phenyl side group (STFPEEK).

Experimental

Materials

3-trifluorophenylhydroquinone was synthesized as described in the literature^[8]. 4,4'-Difluorobenzophenone was purchased from Yanbian chemical factory. Sodium 5,5'-carbonylbis(2-fluorobenzene-sulphonate) was prepared according to a procedure described by Wang et al.^[9] Tetramethylene sulfone (TMS) was purchased from Jizhou Oil Refinery and then purified by distillation under reduced pressure. K₂CO₃ was dried in vacuum for 24h at 150°C.

Synthesis of polymer

A typical reaction is presented for STFPEEK20. (3-Trifluoromethyl)phenylhydroquinone(5g,0.02mol), 4,4'-Difluorobenzophenone(3.43g,0.016mol), Sodium 5,5'-carbonylbis(2-fluorobenzene-sulphonate)(1.66g,0.004mol) were added to a three-necked flask equipped with a mechanical stirrer, nitrogen inlet, and a Dean-stark trap. Then (3.31g 0.024mol) of dried potassium carbonate and TMS was added into the reaction flask. Toluene was used as azeotrope water. The reaction mixture was refluxed at 140°C for 3h to dehydrate the system. Then the temperature was slowly increased to 180°C with the toluene removed and held constant for 4h. The viscous reaction solution was poured into large amount of ice water. The precipitated copolymer was washed several times with deionized water and methanol respectively. Finally, it was dried at 100°C for 24h.

Measurement

The viscosities were measured with Ubbelohde viscosimeter thermostated at 25°C. The polymer concentration was 0.5g/dl in DMAc. IR spectra (KBr pellets or films) were measured on a Nicolet Impact 410 Fourier transform infrared (FTIR) spectrometer. ¹H-NMR experiments were carried out on a Bruker 510 spectrometer (500MHz for ¹H) using d-DMSO as solvent. Differential scanning calorimetry (DSC) measurements were performed on a Mettler Toledo DSC821e instrument at a heating rate of 20 °C/min. The glass-transition temperature (*T_g*) was taken in DSC curve as the center of the step transition in the second heating run. (TGA) measurement was performed on a Netzsch Sta 449c thermal analyzer system at a heating rate of 10 °C/min in air.

Results and Discussion

Copolymerization and characterization

Polymers with different DSs (degree of sulfonation) were obtained in good yields by aromatic nucleophilic substitution by variations in the feed ratio of the monomers. The reaction sequence is depicted in Figure 1. In this article the copolymers are named as STFPEEK-X, where X refers to the molar percentage of the Sodium 5,5'-carbonylbis(2-fluorobenzene-sulphonate).

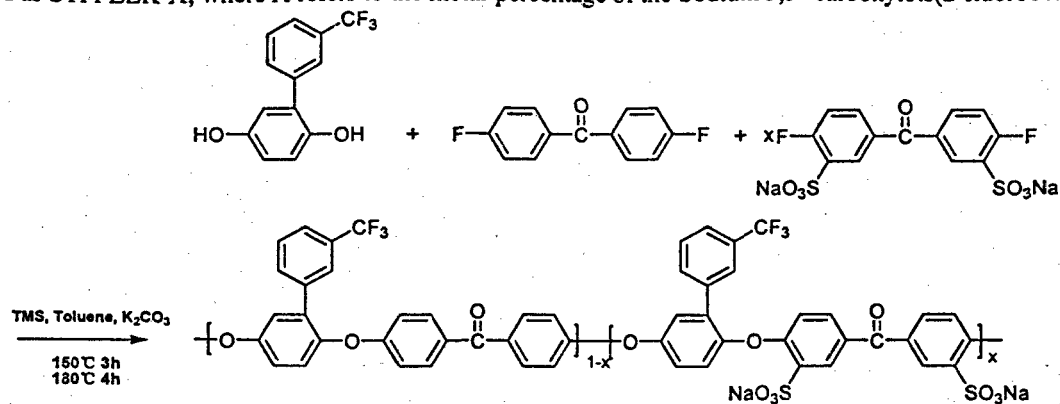


Figure 1. Synthesis of STFPEEK

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Table 1

	X(mol %)	Yield(%)	[μ](dl/g)	DS	Tg(°C)
SF20	20	94	1.51	0.35	159
SF30	30	91	1.52	0.59	189
SF40	40	90	1.47	0.81	ND

ND: not detected below 350°C

The solubilities of sulfonated polymers in some organic solvent are compiled in table 2. These sulfonated copolymers are soluble in strong polarity aprotic solvents such as DMAc, DMSO and NMP. With the rise of the content of sulfonate group, the solubility of copolymers in water and methanol creased also. The DSC data (list in Table 1) showed that the Tgs of the copolymers increased with the rise of the DSs of them. The introduction of sulfonate groups to polymer increased intermolecular interaction by pendant ions and increased molecular bulkiness. Both the two effects hinder internal rotation of the polymer chain, leading to increased glass transition temperature for sulfonated polymers.

Table 2

	H ₂ O	CH ₃ OH	DMAc	DMSO	NMP	CHCl ₃
SF20	-	-	+	+	+	-
SF30	-	-	+	+	+	-
SF40	±	±	+	+	+	-

+ Soluble, - insoluble, and \pm swollen

Conclusion

A series of novel sulfonated PEEK containing (trifluoromethyl)phenyl side group were successfully synthesized, and the degree of sulfonation were well controlled by adjust the feed ratio of sulfonated monomer to unsulfonated monomer. Some pilot studies of their properties were conducted. These copolymers have relative high molecular weights and good solubilities in DMAc, DMSO and other organic solvents, so they may have potential applications in film materials.

Notes

- [1] Bishop, M. T.; Karasz, F. E.; Russo, P.S.; Langley, K. H. *Macromolecules* 1985, 18, 86.
- [2] Maria. Gil, X. L. Ji, X. F. Li, H. Na, J. Eric. Hampdey, Y. F. Lu. *J Membr Sci* 234: 75-81, 2004.
- [3] I. J. Choi, C. J. Ahn, T.H.Yoon. *J Appl Polym Sci* 93:1211-1218, 2004.
- [4] F. Wang, Michael. Hichner, Y.S.Kim, ThomasA. Zawodzinski, James.E.McGrath. *J.Membr.Sci* 197, 231-242, 2002.
- [5] Y. Z. Meng, S. C. Tjong, S. J. Wang, A. S. Hay. *J Polym.Sci. Part A: Polym. Chem* 39, 3218, 2001.
- [6] Miyatake. K, Shoyji, E, Yamamoto. K, Tsuchida. E. *Macromolecules* 1997, 30, 2941.
- [7] Y.Gao, Gilles P. Robertson, Michael D.Guiver, X.Jian, Serguei D.Mikhailenko, K.P.Wang, Serge Kaliaguine, J. J. Polym Sci Part A: Polym Chem 41:2731-2742, 2003.
- [8] B.J. Liu, G.B. Wang, W.Hu, Y.H. Jin, Z.H. Jiang, *J. Polym Sci Part A: Polym Chem* 40:3392-3398, 2002.
- [9] F. Wang, T.L.Chen, J.P. Xu, *Macromol. Chem. Phys.* 199, 1421-1426, 1998.