THE STUDY OF SOLUBLE AND CONTROLLABLE CROSSLINKING POLY (ARYL ETHER ETHER KETONE)S

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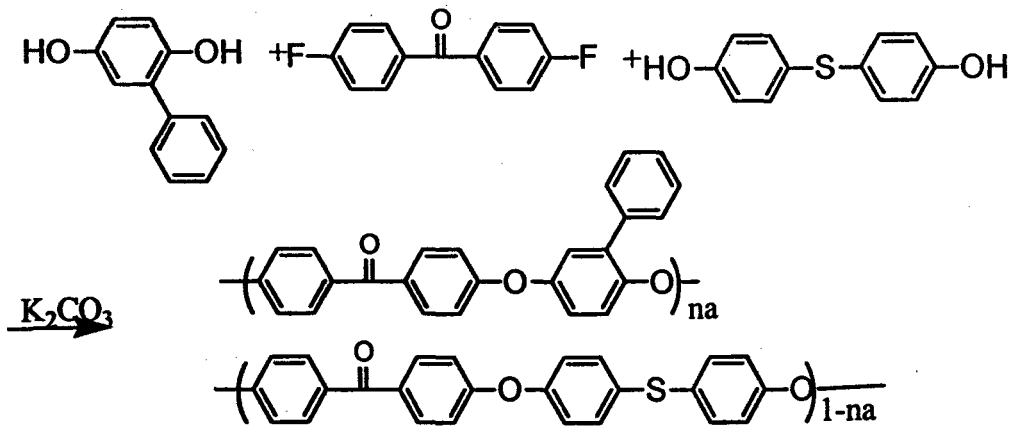
Introduction

Ploy (aryl ether ketone)s (PAEK) are one of the most well-known series of high performance engineering thermoplastic, which have been found very useful as advanced materials due to their excellent thermal stability and good chemical resistance[1] with important application in many high-technology fields, such as nuclear industry, aerospace field, transportation and building materials. Just the excellent properties of polymers of PAEKs restrict the use of PAEKs as membrane material and encapsulation material because PAEKs have high melt viscosity and can be only dissolved in concentration sulfuric acid. In order to obtain different properties of PAEKs, bulky-substituent group were designed and synthesized and introduced into main chain of PAEKs. These polymers were amorphous and can be easily solved in common organic solvents.[2] When did so, another problem appears that the membrane material or encapsulating material can not be destroyed during the process of using by chemical solvents. Therefore, thioether bonds were introduced into soluble PAEKs, in which sulfur acts as a crosslinking points. Materials of PAEKs can be transformed into thermosetting plastic. That is to say, these polymers combined the virtues of thermoplastic materials and thermosetting plastic materials, which can be made contour machining as thermoplastic and used as thermosetting plastic.

The solubility of these polymers depends on not only the initial monomers but also depends on the synthetic methods. It was found that the block copolymer was soluble while the random copolymer was insoluble though they share the same components. We found that the length of thioether block can be controlled and the degree of crossinking can be controlled.

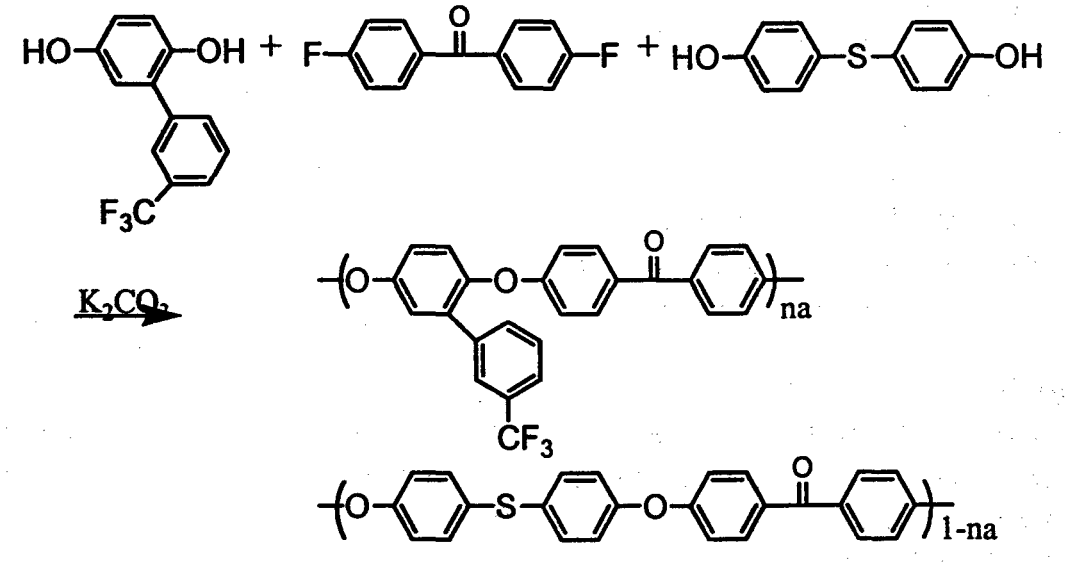
Synthesis

Copolymer was prepared through the nulcleophilic substitution displacement reaction with various phendiol and activated difluoro monomer 4-4'difluorobenzophenone and 4-4'thiodiphenol with K_2CO_3 as base (scheme 1 and scheme 2). Cycle-butyl-sulphone ($TMSO_2$) was used as a solvent at 220°C for reaction. .



Scheme 1. Synthesis of soluble PEEKSK

The block copolymer was synthesized though adding the monomer in different reaction period, which result the polymer soluble. While the synthesis of random copolymer was put all reaction monomers into flask at the same time, which result the polymer insoluble.



Scheme 2. Synthesis of soluble PEEFKSK

Results and Discussion

A series of block and random copolymers have been synthesized and theirs solubility has been studied (table 1). The density of crosslinking point of block copolymer can be controlled by controlling the addition of thioether and the distribution of crosslinking point can be controlled by synthesis method.

Table 1. Solubility behavior of block and random copolymer

Solvent	DMF	DMA	THF	Dichloromethane	Chloroform	Sulfuric acid
Block copolymer	S	S	S	S	S	S
Random copolymer	I	I	I	I	I	S

S stands for soluble, I stands for insoluble

References

(1) Jones D. P.; Leach D. C.; Moore D. R.; *Polymer*. **1985**, 26, 1385.

(2) Gao Zihong; Ben Teng; Liu Xincai; Cao Hui; Qiu He; Wei Zhanhai; Chen Chunhai; Wu Zhongwen; Zhang Wanjin.* *Polymer preprints*, **2000**, 41(2), 1317