Synthesis and Characterization of Novel Soluble Fluorine-containing Poly(aryl ether ketone)s

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Abstract

The novel bisphenol monomer with (3,5-ditrifluoromethyl)phenyl group was synthesized. The structure of bisphenol was confirmed by MS, FTIR and ^{1}H-NMR. Aromatic 6F-PEEK and 6F-PEEKK, based on the bisphenol, were prepared by the aromatic nucleophilic substitution. The results of FTIR and ^{1}H-NMR were agreed with the structure of 6F-PEEK and 6F-PEEKK. Their Tgs were 150°C and 163°C, respectively. The polymers showed good solubility and high thermal stability. The properties of 3F-PEEK and 3F-PEEKK were discussed, too.

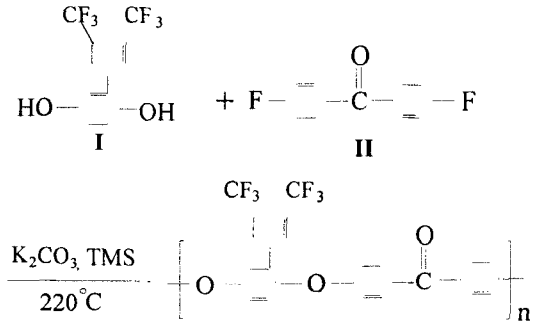
Introduction

Poly(aryl ether ketone)s (PEK's) are a class of high performance engineering thermoplastics known for their good thermal stability, excellent electrical and mechanical properties. This kind of advanced materials are widely studied for their potential application in aerospace, automobile, electronics, and other high technology fields.[1-3] Considerable attention has been devoted to the preparation of fluorine-containing polymers because of their unique properties and high performance. The incorporation of fluorine atoms into the chains leads to polymers with increased solubility, flame resistance, thermal stability, resistance to water and electrical insulating properties, while decreasing color, crystallinity, dielectric constant and moisture absorption.[4-5] The fluorine-containing polymers have currently been used as films, coatings for optical and microelectronics devices, gas separation membranes, matrix resins in fibre-reinforced composites.[6-7] In this paper, we designed and synthesized a kind of novel fluorinated bisphenol monomer. 6F-PEEK and 6F-PEEKK, based on the monomer, were prepared by the aromatic nucleophilic substitution reaction.

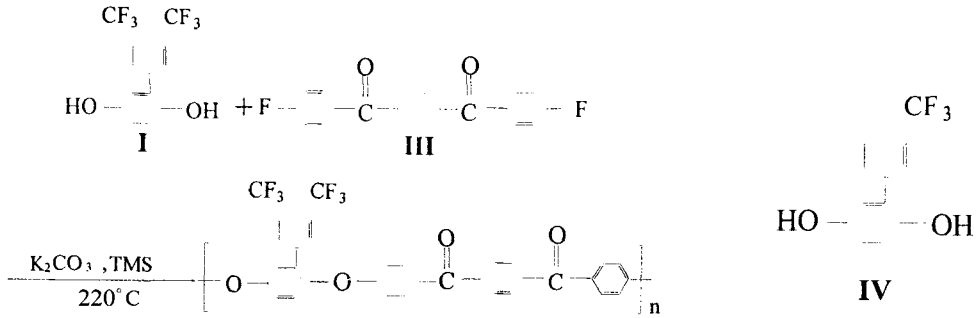
Experimental

Synthesis of 6F-PEEK and 6F-PEEKK

Polymers were synthesized by nucleophilic reaction of difluoromonomers and bisphenols. 32.20g of **I**, 21.80g of **II** (or 32.20g of **III**), calculated anhydrous potassium carbonate, Tetramethylene sulfone (TMS) and toluene were placed in a 500ml three-necked flask equipped with Dean Stark trap, condenser, mechanical stirrer and nitrogen inlet tube. The mixture was allowed to react at reflux for 2h. The toluene was removed by distillation. The polymerization was completed at 220°C after 4h. The mixture was poured into 3000ml of deionized water. The polymer was pulverized into powder after cooling. The powder was distilled in alcohol and water several times and dried at 120°C for 10h. The white polymer powder was obtained finally.



Scheme 1. Synthesis of 6F-PEEK



Scheme 2. Synthesis of 6F-PEEKK

Results and Discussion

1. Structure of monomer.

The bisphenol monomer (**IV**) was previously synthesized by our lab.[8] Based on the monomer (**IV**), a kind of novel bisphenol monomer (**I**) with (3,5-ditrifluoromethyl) phenyl group was designed and synthesized. The structure of monomer (**I**) was confirmed using FTIR, ^{1}H-NMR and MS data. FTIR (KBr) showed 3316cm^{-1}(-OH), 1132cm^{-1}(-CF_3) and other characteristic absorption. **Figure1** showed the ^{1}H-NMR spectrum of monomer (**I**). δ_H ($CDCl_3$):

4.66 ppm (2.0H, H_1+ H_2), 6.82 ppm (1.0H, H_3), 6.79 ppm (1.0H, H_4),

6.81 ppm (1.0H, H_5), 8.00 ppm (2.0H, H_6+ H_8), 7.85 ppm (1.0H, H_7).

MS (9.3ev) showed m/z (%): 322 (100) [M^+]. The melting point (m.p.) of monomer was 113-114°C.

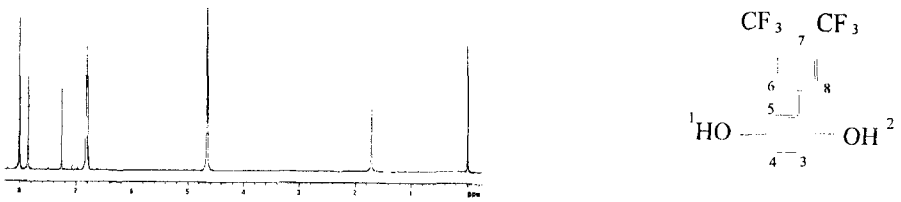


Figure 1. ^{1}H-NMR of monomer

2. Structure of 6F-PEEK and 6F-PEEKK

The results of FTIR and ^{1}H-NMR were agreed with the structure of polymers. The FTIR of 6F-PEEK showed 1663cm^{-1}(-CO-), 1224cm^{-1}(-O-) and 1134cm^{-1}(-CF_3-). The FTIR of 6F-PEEKK showed 1658(-CO-), 1224 cm^{-1} (-O-), and 1132 cm^{-1} (-CF_3). **Figure 2** was the ^{1}H-NMR spectrum of 6F-PEEK. δ_H ($CDCl_3$):

6.90ppm(2.0H, H_1+$H_{1'}$), 7.85 ppm (1.0H, H_2), 7.78 ppm (1.0H, $H_{2'}$),
7.73 ppm (1.0H, H_3), 7.65 ppm (1.0H, $H_{3'}$), 7.11 ppm (2.0H, H_4+$H_{4'}$),
7.21 ppm (1.0H, H_5), 7.22 ppm (1.0H, H_6), 7.20 ppm (1.0H, H_7),
7.97 ppm (2.0H, H_8+H_{10}), 7.80 ppm (1.0H, H_9).

Figure 3 showed the ^{1}H-NMR spectrum of 6F-PEEKK.δ_H($CDCl_3$):

6.93 ppm (2.0H, H_1+$H_{1'}$), 7.91-7.77ppm(8.0H, H_2+$H_{2'}$+H_3+$H_{3'}$+H_4+$H_{4'}$+H_5+$H_{5'}$),
7.14 ppm (2.0H, H_6+$H_{6'}$), 7.25 ppm (1.0H, H_7), 7.29 ppm (1.0H, H_8),
7.24 ppm (1.0H, H_9), 7.97 ppm (2.0H, H_{10}+H_{12}), 7.80 ppm (2.0H, H_{11}).

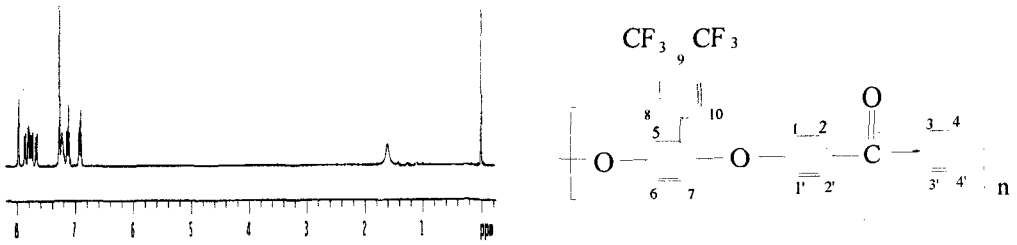


Figure 2. ^{1}H-NMR of 6F-PEEK

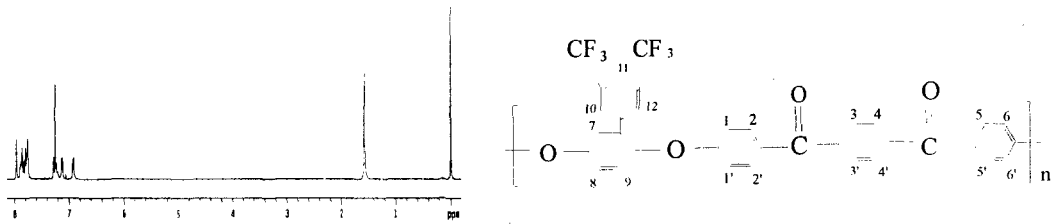


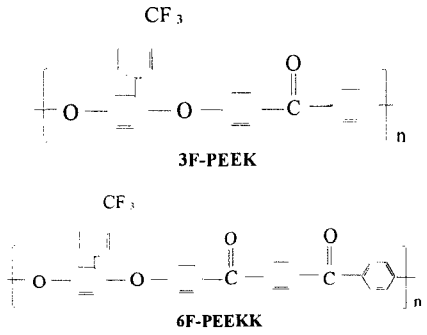
Figure 3. ^{1}H-NMR of 6F-PEEKK

3. Properties of Polymers

Table 1. Properties of Polymers.

polymer	Time of Polymeri-zation	Inherent viscosity (η_{iv})	Tg[c] (°C)	Td[d] (°C)	film	WAXD pattern
6F -PEEK	4h	0.45[a]	150	>500	Flexible transparent	amorphous
6F -PEEKK	4h	0.41[b]	163	>500	Flexible transparent	amorphous
3F- PEEK	4h	0.50[a]	135	>500	Flexible transparent	amorphous
3F- PEEKK	4h	0.81[b]	147	>500	Flexible transparent	amorphous

a. of a 0.1g/10ml solution in DMF, dl/g.
b. of a 0.1g/10ml solution in conc. sulfuric acid, dl/g.
c. glass transition temperature determined by DSC at a scan rate of 20K/min under nitrogen.
d. Temperature at which a 10% weight loss was recorded by TGA at a heating rate of 10K/min in air.



Scheme 3

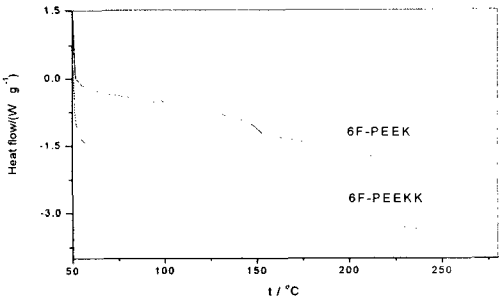


Figure 4. DSC traces of 6F-PEEK and 6F-PEEKK.

The thermal behavior of polymers was evaluated by DSC (**Figure 4**) and TGA. The galss transition temperatures (Tgs) of 6F-PEEK and 6F-PEEKK were 150°C and 163°C, respectively. The polymers were amorphous by the results of DSC and WAXD. 3F-PEEK and 3F-PEEKK(**Scheme 3**)were synthesized based on the monomer (**IV**).[8] **Table 1** was some properties of polymers. A comparison of DSC results for 6F-PEEK and 3F-PEEK showed that incorporation of another fluoromethyl group resulted in a relative highering of Tg by 15°C. This was attributed to the presence of more bulky pendant groups which increased steric hindrance despite the internal plasticization effect of fluorine atoms. The thermal stability of the polymers was studied by TGA. The results were listed in **Table 1**. It was found that all the polymers had high thermal stability. The Td temperatures at which a 10% weight loss in air was recorded were over 500°C.

Regardless of the fluorine content, all the polymers dissolved in DMF, DMAC, NMP, THF, chloroform and dichloromethane. The high solubility behavior should be ascribed to the decrease of the energy and also to the reduction in both polymer chain packing and regularity due to the incorporation of the bulky pendant groups. Strong, transparent and flexible films were easily prepared by their solutions or molding compression.

Conclusions

The fluorine-containing bisphenol monomer with bulky pendant group was synthesized and characterized. The novel 6F-PEEK and 6F-PEEKK were prepared and characterized. Some properties of 3F-PEEK and 3F-PEEKK were discussed, too. All the polymers had high thermal stability and good solubility. Strong, transparent and flexible films were easily prepared. This kind of soluble fluorine-containing PEK's were thought to be promising materials for fields in microelectronics and optical devices. The further work is continuing.

References

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