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Methylated and Trifluoromethylated Aromatic Poly(ether sulfone)s

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Summary

Four aromatic poly(ether sulfone)s (PESs) based on (3-methyl)phenylhydroquinone, (3-trifluoromethyl)phenylhydroquinone, (3,5-dimethyl)phenylhydroquinone, and (3,5-ditrifluoromethyl)phenylhydroquinone were prepared via a nucleophilic aromatic substitution polycondensation with bis(4-fluorophenyl) sulfone. These PESs had a high thermal stability with a 5% weight loss above 423 °C in N_2. The PESs possessed good solubility in common organic solvents. All the polymers formed transparent and flexible films using solution casting method. The dielectric constants estimated from refractive indices of the PES films are 2.64-3.07. Compared with the corresponding methylated PESs, the trifluoromethylated PESs exhibited low glass transition temperatures, higher thermal decomposition temperatures, and low dielectric constants.

Introduction

Aromatic poly(ether sulfone)s (PESs) are a class of high performance thermoplastics known for their unique combination of attractive chemical and physical properties. Several PESs were commercialized and widely used in aerospace, automobile, and electronics fields [1-3]. To obtain the different properties and widen their applications, numerous efforts have been made to prepare functional PESs by either direct polymerization from functionalized monomers or by further reaction from commercial PESs [4,5].

There has been a continuous demand for high-temperature materials for use in microelectronic devices, such as the substrates for printed boards, insulating materials as interlayer dielectrics and intermetal dielectrics, and coatings as electronic packaging. Therefore, the aromatic polymers, such as polyimides, polyethers, poly(ether ketone)s and polybenzoxazoles, with a low dielectric constant, high thermal stability, and good solubility have been widely investigated [6,7].

Because of the unique characteristics of fluorine substitution, fluorinated polymers have been intensively explored as microelectronic devices, optical wave-guide materials, and gas-separation membranes. Fluorine incorporation has been found to generally lower the dielectric constant and moisture absorption, to improve the optical properties, and also to increase the thermal stability. For the fluorinated monomers are relatively hard and expensive to obtain, few are commercially available [8-10]. The introduction of methylphenyl groups on the polymer chains may enhance the solubility and transfer into other functional groups [11].

We are interested in the synthesis of aromatic polymers with fluorinated bulky pendant groups [12,13]. In the present article, we report the successful preparation of four aromatic PESs containing methyl/trifluoromethyl and dimethyl/ditrifluoromethyl phenyl substituents.

Experimental section

Materials

Bis(4-fluorophenyl) sulfone was obtained from Tokyo Kasei Kogyo Co. LTD. Anhydrated 1-methyl-2-pyrrolidinone (NMP) was purchased from Wako Pure Chemical Industries LTD. (3-Methyl)phenylhydroquinone (3H-PH), (3-trifluoromethyl)phenylhydroquinone (3F-PH), (3,5-dimethyl)phenylhydroquinone (6H-PH) and (3,5-ditrifluoromethyl)phenylhydroquinone (6F-PH), were synthesized according to a reported procedure in our lab [12,15]. The other reagents were used as received.

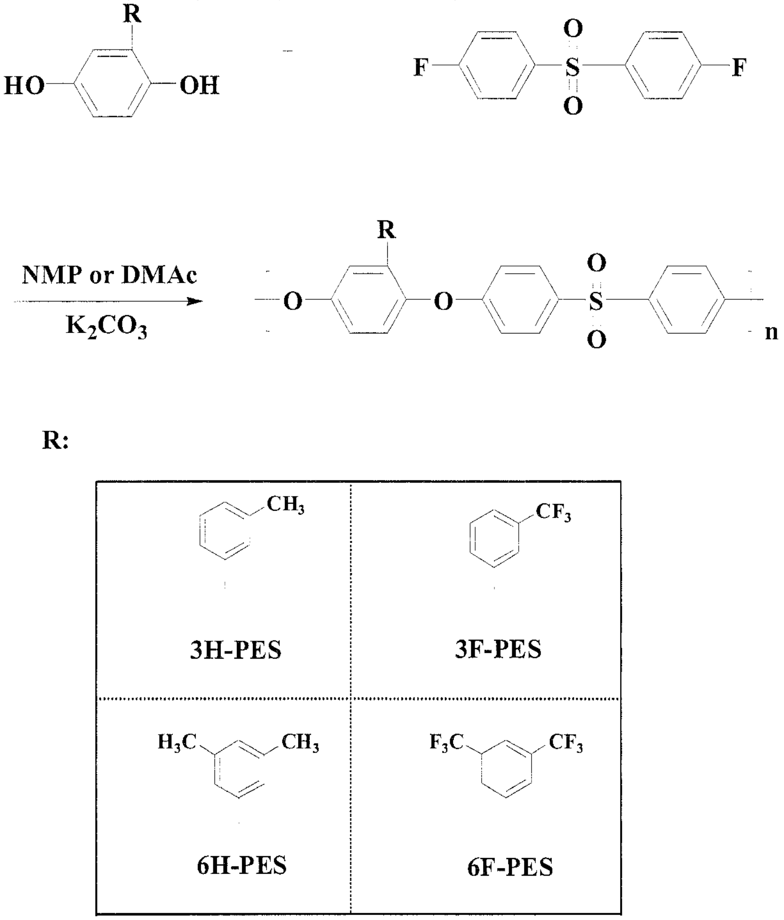
Measurements

FTIR spectra were measured on a JASCO VALOR III Fourier transform spectrometer. ^{1}H NMR spectra were recorded on a JEOL JNM LA-500 spectrometer, and the proton signals in the ^{1}H NMR spectra were assigned in the H,H-COSY spectra. Inherent viscosities (η_{iv}) were measured with an Ostwald viscometer in a 0.5g/dL DMAc solution of the PESs at 30 °C. Differential scanning calorimetry (DSC) measurements were performed on a TA Instrument 2920 DSC at a heating rate of 20°C/min under nitrogen. The glass transition temperature (Tg) was taken in the DSC curve as the center of the step transition in the second heating run. Thermogravimetric analysis (TGA) was performed on a Seiko SSC 5200-TG/DTA 220 thermal analyzer system at a heating rate of 10°C/min under nitrogen. The wide-angle X-ray diffractometer (WAXD) patterns were measured on a Rigaku D/Max-γA X-ray diffractometer with graphite-monochromated Cu*K*α radiation. The refractive indices (n_{ref}) of the polymer films (prepared by spin-coating of polymer solution in chloroform) were obtained using a Gaertner L116B spectroscopic ellipsometer at 632.8 nm.

Polymer synthesis

Poly(ether sulfone) with a (3,5-dimethyl)phenyl group (6H-PES)

To a 50-mL three-necked flask equipped with a magnetic stirrer, a nitrogen inlet with a thermometer, and a Dean-Stark trap with a condenser, were added 6H-PH (1.0713g, 5mmol), bis(4-fluorophenyl) sulfone (1.2713g, 5mmol), anhydrous K_2CO_3 (0.8280g, 6mmol), NMP (10ml) and calculated toluene. The system was allowed to stir and reflux for 2 h under a flow of nitrogen, and then the toluene was removed. The reaction mixture was heated to 165-170°C. After 4 h, the polymerization was complete. The viscous solution was then poured into deionized water. The flexible threadlike polymer was pulverized into powder using a blender. The polymer powder was washed several times with hot water and methanol, and dried at 120°C for 6h.
IR (film, cm^{-1}): 1322, 1152(-SO_2-), 1230 (Ar-O-Ar).
^{1}H NMR ($CDCl_3$, δ, ppm): 7.88 (d, J=8.85Hz, 1H), 7.83 (d, J=8.85Hz, 1H), 7.77(d, J=8.85Hz, 1H), 7.72 (d, J=8.85Hz, 1H), 7.13 (s, 1H), 7.07-7.04(m, 2H), 7.00-6.97(m, 3H), 6.89-6.85(m, 4H), 2.21 (d, J=4.90Hz, 6H).



Scheme 1. Synthesis and structures of novel aromatic poly(ether sulfone)s.

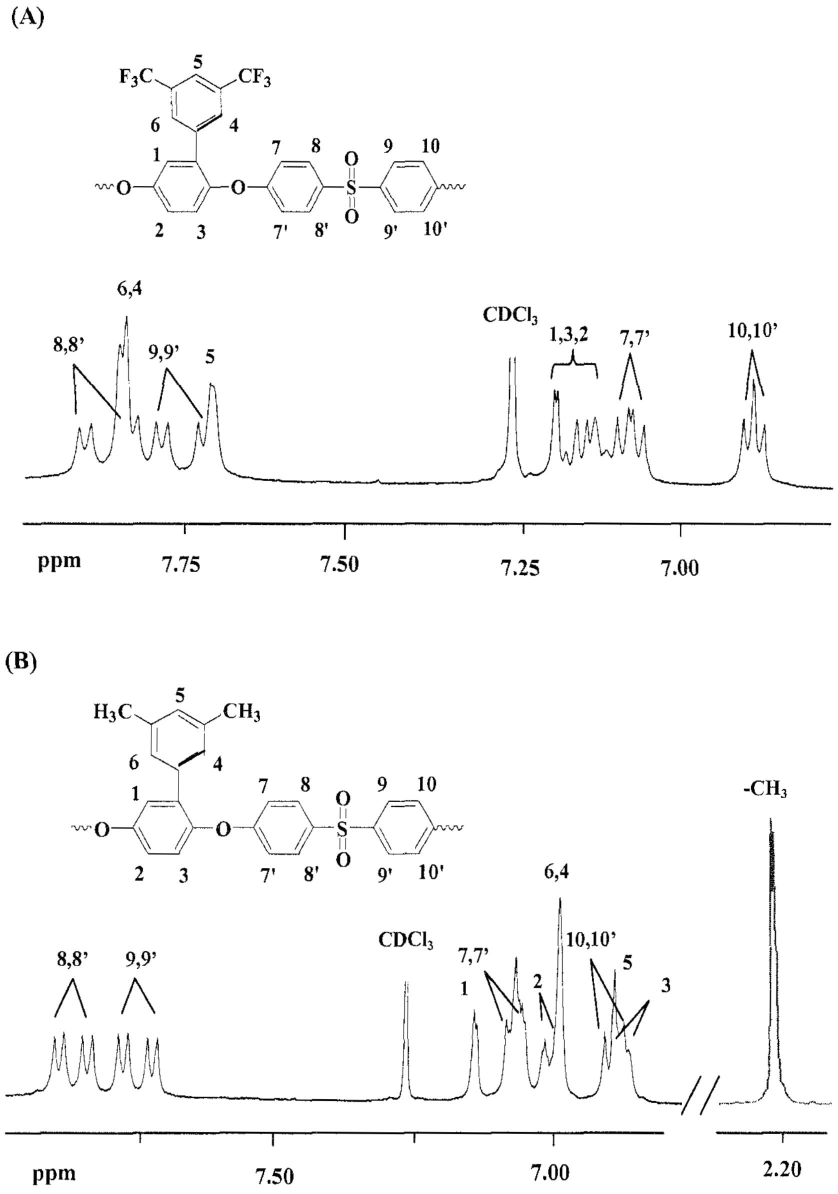


Figure 1. ^{1}H NMR spectra of 6F-PES (A) and 6H-PES (B) ($CDCl_3$).

Poly(ether sulfone) with a (3-methyl)phenyl group (3H-PES)

3H-PES was synthesized by the polymerization of 3H-PH with bis(4-fluorophenyl) sulfone. The procedure is similar to the synthesis of 6H-PES.
IR (film, cm^{-1}): 1322, 1151($-SO_2-$),1230 (Ar-O-Ar).
^1H NMR ($CDCl_3$, δ, ppm): 7.89 (d, J=8.85Hz, 1H), 7.84 (d, J=8.85Hz, 1H), 7.77(d, J=8.85Hz, 1H), 7.72 (d, J=8.85Hz, 1H), 7.17-7.01(m, 9H), 7.00 (d, J=8.85Hz, 1H), 6.87(d, J=8.85Hz, 1H), 2.25 (d, J=3.65Hz, 3H).

Poly(ether sulfone) with a (3-trifluoromethyl)phenyl group (3F-PES)

3F-PES was prepared from 3F-PH and bis(4-fluorophenyl) sulfone according to the same procedure used for 6H-PES.
IR (film, cm^{-1}): 1333, 1152($-SO_2-$), 1229 (Ar-O-Ar), 1125 ($-CF_3$).
^1H NMR ($CDCl_3$, δ, ppm): 7.90 (d, J=8.85Hz, 1H), 7.84 (d, J=8.85Hz, 1H), 7.78(d, J=8.85Hz, 1H), 7.71 (d, J=8.85Hz, 1H), 7.66(s,1H), 7.56 (d, J=9.15Hz, 1H), 7.47(t, J=8.85Hz, 1H), 7.39(m, 1H), 7.17 (s, 1H), 7.13-7.05(m, 4H), 6.88(d, J=8.85Hz, 1H), 6.86(d, J=8.85Hz, 1H).

Poly(ether sulfone) with a (3,5-ditrifluoromethyl)phenyl group (6F-PES)

6F-PES was synthesized by the polymerization of 6H-PH with bis(4-fluorophenyl) sulfone. DMAc was used as solvent.
IR (film, cm^{-1}): 1324, 1152($-SO_2-$) , 1228 (Ar-O-Ar), 1130 ($-CF_3$).
^1H NMR ($CDCl_3$, δ, ppm): 7.91 (d, J=8.85Hz, 1H), 7.85(s, 2H), 7.84 (d, J=8.85Hz, 1H), 7.79(d, J=8.85Hz, 1H), 7.73 (d, J=8.85Hz, 1H), 7.72(s, 1H), 7.19-7.11(m, 3H), 7.08(d, J=8.85Hz, 1H), 7.06(d, J=8.85Hz, 1H), 6.89(d, J=8.85Hz, 1H), 6.87(d,J=8.85Hz, 1H).

Results and discussion

Polymer synthesis

The nucleophilic aromatic substitution polymerization of four novel bisphenols with bis(4-fluorophenyl) sulfone was carried out in the presence of K_2CO_3 after removing the water from the reaction system by the azeotropic distillation of toluene, as shown in Scheme 1. The poly(ether sulfone)s with high molecular weights were obtained in 4 h. The inherent viscosities of the resulting polymers ranged from 0.36 to 1.10 dL/g in DMAc at 30 °C, as shown in Table 1.

FTIR and NMR spectroscopies were performed to confirm the structures of the resulting polymers. In the FTIR spectra of the polymer films, the characteristic absorption bands around 1322 and 1150 cm^{-1} due to sulfonyl groups, and around 1230 cm^{-1} based on aryl ether linkages. The FTIR spectra of 3F-PES and 6F-PES showed the absorption bands around 1130 cm^{-1} corresponding to trifluoromethyl moieties. The results of ^1H NMR spectra were well agreed with the proposed structures of polymers. The signals at 7.91-6.85 ppm are assigned to the aromatic protons in the molecular chains. Some differences between the chemical shifts of the corresponding protons beside the sulfonyl moieties were caused by the asymmetric substitution of the side groups. Compared with trifluoromethylated polymers, the spectra of methylated polymers showed the unique absorptions about 2.20 ppm due to methyl groups. The typical ^{1}H NMR spectra of 6F-PES and 6H-PES with comparable structures are illustrated in Figure 1.

Table 1. Inherent viscosities (η_{iv}) and properties of polymers

Polymer	η_{iv} (dL/g) [a]	Tg (°C) [b]	DT_5 (°C) [c]	DT_{10} (°C) [d]	n 632.8nm [e]	ε_{opt} [f]
3H-PES	0.36	176	423	447	1.67	3.07
3F-PES	0.45	167	507	530	1.64	2.96
6H-PES	0.52	190	428	446	1.65	2.99
6F-PES	1.10	176	498	515	1.55	2.64

a. Measured at a polymer concentration of 0.5 g/dL in DMAc at 30 °C.

b. From the second heating trace of DSC measurements conducted at a heating rate of 20 °C min^{-1}.

c. 5% weight loss temperatures measured by TGA at a heating rate of 20 °C min^{-1} in N_2.

d. 10% weight loss temperatures measured by TGA at a heating rate of 20 °C min^{-1} in N_2.

e. Refractive index at 632.8 nm.

f. Dielectric constant estimated from the refractive index at 632.8 nm: $\varepsilon_{opt} = 1.10\,n^2$.

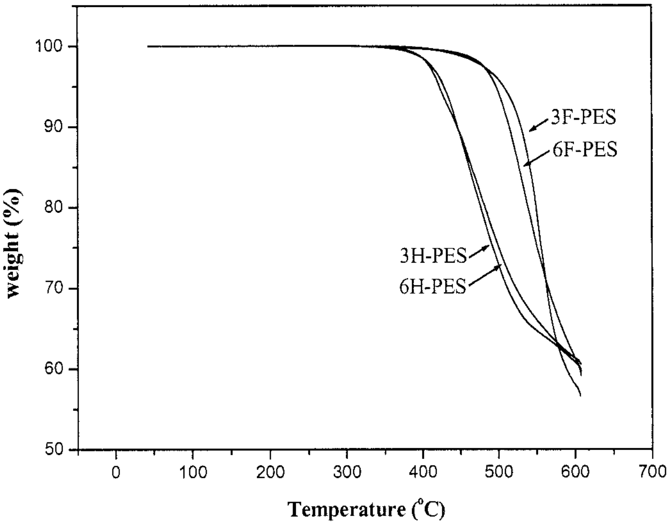


Figure 2. TGA curves of the polymers in nitrogen.

The crystallinity of the poly(ether sulfone)s was evaluated by wide-angle X-ray diffraction (WAXD). As expected, all the polymers exhibited amorphous patterns due to their irregular molecular structures.

Thermal properties of polymers

The thermal properties of the polymers were evaluated by DSC and TGA, as summarized in Table 1. The Tg values of 3H-PES, 3F-PES, 6H-PES and 6F-PES were 176°C, 167°C, 190°C, and 176°C, respectively. It is interesting to observe that the Tg's of the trifluoromethylated PES's were lower than their corresponding methylated PES's as follows: 3F-PES < 3H-PES and 6F-PES < 6H-PES, respectively. That the substitution of methyl group with trifloromethyl group would lead to an internal plasticization in addition to the other factors was suggested to explain this phenomenon [14,15]. No melting endotherms were observed in the DSC traces, which further confirmed the amorphous nature of the polymers.

The polymers had good stability against thermal decomposition, as summarized in Table 1. The temperatures at a 5% weight loss (TD_5) are above 423°C and the temperatures at a 10% weight loss (TD_{10}) are above 446°C in nitrogen. As anticipated, the fluorinated 3F-PES and 6F-PES exhibited a higher thermal stability than the nonfluorinated 3H-PES and 6H-PES. A comparison of TGA curves was given in Figure 1. This is due to the stronger C-F bonds in comparison of C-H bonds.

Solubility and dielectric constants of the polymers

These polymers exhibited good solubility in common organic solvents (Table 1). All of them were soluble at room temperature in aprotic polar solvents such as NMP, DMAc and DMF as well as in the less polar solvents such as chloroform and tetrahydrofuran (THF). The good solubility of the polymers could be attributed to the introduction of the asymmetrical bulky substituents, which disturb the close packing of the polymer chains and lead to the increased free volume. Therefore, it will become easy for solvents to solubilize the polymer chains. All the polymers could form transparent and flexible films by solution casting.

Table 2. Solubility of the polymers

Polymers	$CHCl_3$	THF	DMF	DMAc	NMP
3H-PES	++	++	++	++	++
3F-PES	++	++	++	++	++
6H-PES	++	++	++	++	++
6F-PES	++	++	++	++	++

++ = soluble at room temperature

$CHCl_3$: chloroform; THF: tetrahydrofuran; DMF: *N,N*-dimethylformamide; DMAc: *N,N*-dimethylacetamide; NMP: 1-methyl-2-pyrrolidone.

The polymers showed the refractive indices ranged from 1.55 to 1.67 at 632.8 nm. The dielectric constant (ε) of the materials at optical frequencies can be estimated from the refractive index (n) according to Maxwell's equation, $\varepsilon \approx n^2$. The ε around 1 MHz is evaluated to be $\varepsilon \approx 1.1n^2$, including an additional contribution of approximately 10% from the infrared absorption [16,17]. The ε values estimated from the refractive indices of the resulting polymer films were in the range of 2.64-3.07, as summarized in Table 1. It is obvious that the trifluoromethylated 3F-PES and 6F-PES had lower dielectric constants than the corresponding methylated 3H-PES and 6H-PES, respectively.

Conclusions

Four aromatic PESs containing methyl/trifluoromethyl and dimethyl/ditrifluoromethyl phenyl substituents were prepared via a nucleophilic aromatic substitution polycondensation. The Tg's of the polymers were in the range of 167-190°C. The fluorinated 3F-PES and 6F-PES exhibited outstanding thermal stability, and their TD_5 and TD_{10} were above 498 and 515 °C in nitrogen, respectively. These polymers have good solubilitiy in common organic solvents, such as DMF, DMAc, NMP, chloroform and THF. The dielectric constants estimated from refractive index of the polymers were 2.64-3.07. In comparison of methylated PESs, the corresponding trifluoromethylated PESs exhibited lower Tg's, higher thermal stability, and lower dielectric constants. Some of the polymers may be considered as good potential candidates for high-temperature electro-optic materials.

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