Synthesis and Property of Poly(arylene sulfone)s Containing 9,9-Diarylfluorene Moiety in the Main Chain

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ABSTRACT: Poly(arylene sulfone)s (**PASs**) were synthesized in quantitative yields by the oxidations of the corresponding fluorene-containing poly(arylene thioether)s, derived from 9,9-diarylfluorene-based dithiols and dihaloarenes, with 30% hydrogen peroxide in formic acid. **PASs** had good solubility in common organic solvents such as chloroform, *N*-methylpyrrolidone (NMP), and *N,N*-dimethylformamide (DMF). Highly transparent films were obtained by casting the chloroform solutions of **PASs**. **PASs** exhibited high glass transition and high decomposition temperatures (T_g 248–355 °C, $T_{d5} > 400$ °C under nitrogen). [doi:10.1295/polymj.PJ2006211]

KEY WORDS Poly(arylene thioether) / Poly(arylene sulfone) / 9,9-Diarylfluorene / Thermal Stability / Solubility /

Increasing interest has been devoted to the syntheses of high performance polymers with special property including poly(arylene sulfone)s as amorphous engineering thermoplastics. Poly(arylene sulfone)s possess excellent properties such as mechanical strength, hydrolytic stability, low flammability, and oxidative stability, making them widely useful in various applications.¹ For example, they could be the basic materials for porous and dense polymeric membranes required for gas separation or fuel cell application.² Some polysulfones are commercially available as high performance engineering plastics such as UDEL[®], VICTREX[®], RADEL[®], and so on. Aromatic polysulfones are often synthesized by direct polymerization *via* aromatic nucleophilic substitution of the corresponding bis(fluoroaryl)sulfones and bisphenols as monomers.³ Ueda *et al.*⁴ have reported the synthesis of aromatic poly(ether sulfone)s from nickel complex-mediated aromatic coupling polymerization of aromatic dichloride. An alternative way of making poly(arylene sulfone)s involves oxidation of poly(arylene thioether)s with hydrogen peroxide in formic acid.^{5,6} By the replacement of thioether function with sulfone function in polymer main chain, it is expected that sulfone polymer shows, *e.g.*, glass transition temperature (T_g) higher than the corresponding thioether polymer. Meanwhile, polymers containing 9,9-diarylfluorene moieties in the main chain have collected much interest because of their excellent properties such as high solubility and good optical properties based on the *cardo* structure of the 9,9-diarylfluorene moiety.⁷ Since polysulfones are usually hard to be soluble in ordinary organic solvents, the introduction of the fluorene skeleton seems

to improve the solubility of polysulfones in addition to endowment of good optical property. We have recently prepared 9,9-diarylfluorene-based poly(arylene thioether)s with excellent physical and optical properties.⁸ As far as we know, no data has been reported by using of poly(arylene thioether)s containing 9,9-diarylfluorene to obtain poly(arylene sulfone)s. Therefore, we have undertaken the synthesis of poly(arylene sulfone)s by the oxidation of the poly(arylene thioether)s, judging from the ease of procedure. This report describes the synthesis and characterization of 9,9-diarylfluorene moiety-based poly(arylene sulfone)s obtained by the oxidation of the corresponding poly(arylene thioether)s.

RESULTS AND DISCUSSION

Synthesis of 9,9-diarylfluorene-based poly(arylene thioether)s (**PTEs**) was carried out by the polycondensation of 9,9-bis(*N,N*-dimethyl-*S*-carbamoylphenyl)-fluorenes and difluoroarenes, according to our previous report.⁸ The structures of the difluoroarenes employed for the **PTE** synthesis are shown in Scheme 1. The yields of **PTEs** were always quantitative. **PTEs** used as starting materials had the molecular weights ranging from 28,800 to 128,000. A series of poly(arylene sulfone)s (**PASs**) were prepared according to Scheme 1 by heating **PTEs** with 30% hydrogen peroxide in 90% formic acid at 50 °C for 2 h. The white solid products were filtrated and washed with methanol to give **PASs** as white fibrous solids in quantitative yield. The comparison of GPC data of **PTEs** and **PASs** suggested little change in molecular weight before and after the oxidation. Although it is

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	Ar	Polymer	R	Polymer	R
a		PTE1 PAS1	H	PTE6 PAS6	Me
b		PTE2 PAS2	H	PTE7 PAS7	Me
c		PTE3 PAS3	H	PTE8 PAS8	Me
d		PTE4 PAS4	H	PTE9 PAS9	Me
e		PTE5 PAS5	H	PTE10 PAS10	Me

Scheme 1.

Figure 1. Selected ^1H -NMR spectrum of PAS5 and PTE5.

not complete comparison due to the structural difference of them and the estimated values based on polystyrene standards, the observed GPC change seems small enough to suggest that the oxidation process does not give rise to the serious change in polymer structure: no cleavage of polymer main chain of **PESs** occurs during the oxidation.

The structures of **PASs** were confirmed by the FT-IR, in which all **PASs** showed characteristic bands around 1150 cm^{-1} and 1320 cm^{-1} due to the stretching vibrations of the SO_2 group. Typical ^1H -NMR spectrum (**PAS5**) is shown in Figure 1. Because of

the strong electron-withdrawing nature of the sulfone groups, the aromatic proton chemical shifts adjacent to the sulfone groups of **PASs** shifted to much lower field compared with those of their precursors **PTEs**. The thermal properties of **PASs** were characterized by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). TGA revealed good thermal stability of **PASs**, which displayed onset decomposition temperature up to 400 and 380°C in nitrogen and air atmospheres, respectively (Figure 2). As shown in Table I, 5% weight loss temperatures (T_{d5}) were in a range of $404\text{--}537^\circ\text{C}$ and $386\text{--}512^\circ\text{C}$ in ni-

Table I. Thermal properties of **PASs** and **PTEs**

Polymer	M_w^a $\times 10^4$	M_n^b $\times 10^4$	T_g (°C) ^c	T_{d5} (N ₂) ^d	T_{d5} (Air) ^d	Polymer	M_w $\times 10^4$	M_n $\times 10^4$	T_g (°C)	T_{d5} (N ₂)	T_{d5} (Air)
PTE1	9.8	4.4	275	553	522	PAS1	9.5	5.2	355	477	473
PTE2	12.8	4.0	217	508	498	PAS2	7.5	3.2	275	493	435
PTE3	3.3	1.6	216	532	519	PAS3	2.6	1.5	290	520	499
PTE4	10.8	3.6	229	551	524	PAS4	8.4	4.0	304	511	512
PTE5	6.1	1.9	212	540	526	PAS5	5.2	2.6	282	537	507
PTE6	3.4	1.6	252	439	447	PAS6	2.8	1.6	296	404	395
PTE7	7.3	2.5	215	448	443	PAS7	4.7	2.1	248	421	387
PTE8	2.9	1.2	212	511	463	PAS8	3.5	1.6	267	410	389
PTE9	3.6	1.7	221	537	474	PAS9	4.2	1.9	280	415	392
PTE10	10.5	3.1	210	466	466	PAS10	10.6	3.8	258	413	386

^a M_w : weight-average molecular weight estimated by GPC based on polystyrene standards. ^b M_n : Number-average molecular weight estimated by GPC based on polystyrene standards. ^cDSC measurement was conducted at a heating rate 10 °C/min in N₂ and air atmosphere. ^dTGA was carried out at a heating rate of 10 °C/min.

Figure 2. Selected TGA thermograms of **PAS1**, **5**, **7** and **9**. Heating rate: 10 °C/min in nitrogen atmosphere.

trogen and air atmosphere, respectively. The thermal stability of **PAS** was always lower than that of the corresponding **PTE** in most cases, probably because **PTE** has thermosetting property in contrast to **PAS**.⁹ The DSC study of **PASs** with a scanning rate of 10 °C/min under a nitrogen atmosphere indicated that all **PASs** were not crystalline but amorphous. The glass transition temperature T_g of **PASs** was in a range from 248 to 355 °C, depending on their structures. Inspection of the data in Table I reveals the T_g s of **PASs** 40–80 °C higher than those of **PTEs**, indicating that the incorporation of the sulfone moiety significantly increases the polymer chain rigidity. **PAS1** which contains oxadiazole moiety on the polymer backbone had the highest T_g of 355 °C, probably due to the enhanced rigidity of **PAS1** by the heterocyclic moiety compared with other **PASs**, indicating the sufficient

rigidity derived by the sulfone function of the **PAS1** structure. Thermal properties of **PASs** were compared with those of commercial polysulfones (Udel®-P1700: T_g 190 °C, T_{d10} 523 °C; PES®-5200P: T_g 220 °C, T_{d10} 555 °C).¹⁰ Since T_g of **PASs** ranges from 282 to 355 °C (for R = H) or from 248 to 296 °C (for R = Me) (Table I), **PASs** have considerably higher glass transition points than the commercial polysulfones, in consistent with their rigid structures. Meanwhile, as for the thermal decomposition points of **PASs**, T_{d10} of them ranges from 498 to 557 °C (for R = H) or from 420 to 447 °C (for R = Me) (Table I shows the data for T_{d5}). Therefore, **PASs** are thermally stable similarly to the commercial polysulfones, if **PASs** have no methyl group on the aromatic rings, although M_w of **PASs** is not optimized. Thus, the introduction of the fluorene skeleton is found to contribute to the

Figure 3. Example of commercial polysulfone.

thermal stability of polysulfones. Solubility of **PASs** is listed in Table II. Despite the fact that **PASs** have the rigid polymer main chains by the sulfone groups which correspond to the high glass transition temperature, **PASs** retained their good solubility in various organic solvents such as chloroform, dichloromethane, NMP, and nitrobenzene. Compared with the corresponding **PTEs** which are insoluble in highly polar solvents such as DMF and DMSO, **PASs** showed good solubility in DMF and DMSO, being in consistent with the high polarity of **PASs**. The high solubility of **PASs** can be attributed mainly to its kink main chain structure involving sp^3 hybridized carbon at the 9-position of the fluorene unit where the molecular space for solvation would be emerged by the perpendicular orientation between the aryl and fluorene moieties. Namely, it is called the “*cardo*” structure of the 9,9-diarylfuorene moiety. **PASs** were insoluble in toluene and THF except for **PAS2** and **PAS7**. It is concluded that low solubility of polysulfone polymer can be improved by the introduction of some groups capable of enhancing solvation such as the 9,9-diarylfuorene moiety producing molecular space. Since **PASs** had good solubility, transparent and strong thin films of **PASs** could readily be prepared by casting from chloroform solution. All films were self-standing and transparent but somewhat brittle.

In comparison with related aromatic poly(thioether) analogue (**PTEs**), the **PASs** films showed slightly higher strong film than their **PTEs** analogues. Figure 4 illustrated some of the UV-vis spectra of the **PASs** films in the wavelength region ranging from 200 to 700 nm. All **PASs** had good transparency in a visible region: the transmittance at 450 nm was over 80%. The cut off wavelength was *ca.* 320–334 nm for **PASs**. The transparency of **PASs** would come from their amorphous nature presumably owing to the *cardo* structure of the fluorene moiety in the main chain. In summary, high performance poly(arylene sulfone)s (**PASs**) containing 9,9-diarylfuorene moiety in the main chain were synthesized *via* the oxidation of poly(arylene thioether)s (**PTEs**) with hydrogen peroxide in formic acid. **PASs** possessed high thermal stability with decomposition temperatures above 400 °C under nitrogen atmosphere. The introduction of the sulfone groups increased the glass transition temperature by 40–80 °C compared with those of the corresponding **PTEs**. **PASs** showed high solubility in spite that they involve the sulfone groups. By casting the **PAS** solution, good transparent thin films were obtained.

EXPERIMENTAL SECTION

Measurements

¹H NMR spectra were recorded on a JEOL GTX-400 spectrometer using CDCl₃ as the solvent with tetramethylsilane as the internal standard. Molecular weight and its distribution were estimated by GPC on a JASCO Gulliver system equipped with two consecutive linear polystyrene gel columns (Tosoh TSKgel G5000H_{XL}, G4000H_{XL}) at 30 °C (flow rate 0.085 mL/min) using polystyrene standards and chloroform as the eluent. The glass transition temperature (*T_g*) was determined with a Shimadzu DSC-60 instrument at a heating rate of 10 °C/min under a

Table II. Solubility of Polysulfones **PASs**^{a,b}

Polymer	Solvent									
	NMP	CHCl ₃	DMAc	THF	CH ₂ Cl ₂	Benzene	Toluene	Nitrobenzene	DMSO	DMF
PAS1	++	+	++	–	+	–	–	++	++	++
PAS2	++	++	++	++	++	±	–	++	++	++
PAS3	++	++	++	–	++	–	–	++	++	++
PAS4	++	++	++	–	++	–	–	++	++	++
PAS5	++	++	++	–	++	–	–	++	++	++
PAS6	++	++	++	–	+	–	–	++	++	++
PAS7	++	++	++	++	++	±	–	++	++	++
PAS8	++	++	++	–	++	–	–	++	++	++
PAS9	++	++	++	–	++	–	–	++	++	++
PAS10	++	++	++	–	++	–	–	++	++	++

^aKey: ++, soluble; +, slowly soluble; ±, partially soluble on heating; –, insoluble. ^bSolubility test was carried out by using 3 mg of polymer and 1 mL of solvent.

Figure 4. Transmittance of **PAS2**, **3**, **4**, **5**, and **6** in film state.

nitrogen flow of 50 mL/min. The thermogravimetric analysis (TGA) was performed with a Shimadzu TGA-50 instrument at a heating rate of 10 °C/min under nitrogen atmosphere and in air atmosphere (flow rate 50 mL/min). Transparency was measured by UV-vis spectroscopy on a JASCO Ubest V-560 spectrophotometer. Solubilities of **PASs** were determined using 3 mg of polymer and 1 mL of solvents. FT-IR spectra were recorded on a JASCO FT-IR-230 spectrophotometer.

Materials

PTEs 1-10 were prepared in quantitative yields according to our previous report.⁸

PTE1 (M_n 44,000, M_w 98,000, MWD 2.3), **PTE2** (M_n 40,000, M_w 128,000, MWD 3.2), **PTE3** (M_n 15,900, M_w 33,000, MWD 2.0), **PTE4** (M_n 36,000, M_w 108,000, MWD 2.8), **PTE5** (M_n 19,000, M_w 60,900, MWD 3.2), **PTE6** (M_n 15,900, M_w 34,000, MWD 2.1), **PTE7** (M_n 25,000, M_w 72,500, MWD 2.9), **PTE8** (M_n 12,000, M_w 28,800, MWD 2.4), **PTE9** (M_n 17,000, M_w 35,700, MWD 2.1), **PTE10** (M_n 31,000, M_w 105,000, MWD 3.4). The reagent and chemicals for preparation of monomer and polymer were purchased from aldirch and used as received without further purification.

Typical Procedure for the Synthesis of Poly(arylene sulfone) (**PAS**)⁶

In a 25 mL round bottom flask, **PTE5** (0.50 g) was suspended in 10 mL of 90% formic acid. To the suspension was added dropwise 5.0 g of 30% hydrogen peroxide at 50 °C. After stirring for 2 h at 50 °C, the white product was filtered, washed with methanol, and dried at 80 °C *in vacuo* for 24 h to give **PAS5**.

¹H NMR (400 MHz, CDCl₃): δ 8.02 (d, 4H, J = 8.1 Hz, Ar-H), 7.84–7.76 (m, 14H, Ar-H), 7.39–7.21 (m, 12H, Ar-H), 7.12 (d, 4H, J = 8.1 Hz, Ar-H). ¹³C NMR (400 MHz, CDCl₃): δ 193.7, 160.2, 151.1, 148.5, 144.3, 140.1, 139.5, 132.7, 132.0, 130.2, 128.9, 128.6, 128.3, 128.0, 127.8, 125.8, 120.7, 118.8, 65.2.

Preparation of Cast Film: General Procedure

One of **PASs** was dissolved in chloroform, so as to give 3 wt % solution. The solution was filtered through membrane filter (pore size 0.45 μ m) and casted on a Teflon plate. The plate was allowed to stand at room temperature for 24 h. The resulting film was further dried in a drying oven at 60 °C for 24 h.

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