Novel Electroactive Poly(arylene ether sulfone) Copolymers Containing Pendant Oligoaniline Groups: Synthesis and Properties

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ABSTRACT: We present a series of novel poly(arylene ether sulfone) copolymers containing pendant oligoaniline groups. A novel monomer containing oligoaniline, 2,6-difluorobenzoyl aniline tetramer (DFAT), was synthesized by reaction of 2,6-difluorobenzoyl chloride and parent aniline tetramer and incorporated into the aforementioned copolymers via direct copolymerization with 4,4'-dichlorodiphenyl sulfone (DCDPS), and 4,4'-isopropylidene diphenol (BPA) using *N*,*N*-dimethylaceta-mide as solvent. The structures of these copolymers were confirmed by FTIR, ¹H NMR, and GPC. Spectral analysis of the copolymers in different oxidation states was investigated via UV-visible spectra. The copolymers exhibited outstanding thermal stability and good solubility in various organic solvents. Their electroactivity, explored with cyclic voltammetry, was

INTRODUCTION Conducting polymers continue to attract great academic and industrial interest in the chemistry, physics, engineering, and material science following the work of Shirakawa and coworkers in the late 1970's on the conducting properties of polyacetylene.¹ In recent years, organic conducting polymers have been studied extensively and have found promising applications in the fields of organic field-effect transistors, photovoltaic cells, light emitting diodes, and sensors.²⁻⁵ Polyaniline (PANI), one of the most frequently investigated conducting polymers, has great potential for advanced applications such as electroluminescent, biosensors, electrochemical capacitors, chemical sensors and electromagnetic interference shielding materials⁶⁻⁸ due to its excellent environmental stability, ease of synthesis and reversible acid/base doping/dedoping chemistry.9-12 However, PANI prepared by chemical and/or electrochemical methods present a number of problems both in academic research and industrial application.^{13,14} First, the ill-defined molecular structure impeded the better understanding of the structure-property correlations and the conducting mechanism of PANI. Second, poor solubility, fusibility, and processability restrict the practical application of PANI. Further, its single functionality has severely limited the expansion of its potential applicability.

found to increase as the content of oligoaniline in the polymer increased. The electric and dielectric properties of the copolymers were also studied in detail. The electrochromic performance of the copolymers was investigated by electrochromic photographs and transmittance spectra; the color of the copolymer thin films changes from grey (at 0.0 V), to green (at 0.4 V), to blue (at 0.6 V) and to pearl blue (at 1.0 V) and the maximum transmittance change (ΔT) at 700 nm is 42.6% (90.7% \leftrightarrow 48.1%). © 2011 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 49: 1605–1614, 2011

KEYWORDS: conducting polymers; copolymerization; electroactive; electrochromic; oligoaniline; poly(arylene ether sulfone); redox polymers

In contrast to PANI, oligoanilines have already been investigated thoroughly due to their structure regularity, good electroactivity, excellent solubility, and excellent processability.^{15–20} However, stability and mechanical properties of oligoanilines are poor compared with those of the analogous polymers. One of the most promising approaches is to prepare functional polymers based on oligoanilines, with welldefined molecular structure, as these should combine the excellent solubility and processability inherent to the oligomers with the mechanical benefits of a macromolecule. Considerable effort has been devoted recently toward chemically synthesizing polymers based on oligoanilines, such as graft, alternating, and block-like polymers. Pron and coworkers^{21,22} copolymerized 3-octylthiophene with thiophene containing tetra-aniline in the 3-position to prepare a hybrid copolymer, which exhibits very interesting spectroscopic and electrochemical properties. Both of the oligoaniline side chains and the polymer main chains could be doped consecutively. Polymers with conjugated aniline oligomers in the main chains have also been prepared by an acid-induced polycondensation.²³ These polymers displayed good solubility in common organic solvents and electrical conductivities up to 0.1 S/cm upon doping with hydrochloric acid. Electroactive polyimides derived from the bis-amino-terminated aniline trimer were

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also reported by Wei and coworkers²⁴ Novel poly(methacrylamide)s containing oligoaniline side chains were prepared by free radical polymerization and its redox behaviors were investigated.²⁵ Many electrochromic polyamides, reported by Wang and coworkers,²⁶ were prepared by the condensation polymerization between amine-capped oligoaniline and acyl chlorides such as isophthaloyl dichloride, terephthaloyl chloride, and azelaoyl chloride. A series of novel electroactive block copolymers with bioactive properties was synthesized by coupling an electroactive carboxyl-capped aniline pentamer with two bioactive bihydroxyl-capped polymers via a condensation reaction.^{27–29} In addition, electroactive poly (aryl ether) materials with oligoanilines in the main chains have been reported in our group,³⁰⁻³² and the materials synthesized by polycondensation or oxidative coupling polymerization displayed excellent thermal stability.

Polymers containing pendant oligoanilines are of interest because the large side groups should simultaneously decrease molecular mobility and enhance solubility. The electrical, electrochemical and mechanical properties can be easily modified by adjusting the feed percent through copolymerization.²⁵ We chose poly(arylene ether sulfone)s as the main chain to attach the pendant olidoanilines. Poly(arylene ether sulfone)s materials are a family of high-performance engineering plastics with excellent properties, such as film formation, thermal and dimensional stability. Functional poly (arylene ether sulfone)s have been well studied as proton exchange membranes, gas-separated membranes, adhesives and optical materials.^{33–35} Herein, we describe the synthesis of a new monomer, 2,6-difluorobenzoyl aniline tetramer (DFAT) and its facile incorporation into poly(arylene ether sulfone) backbones, yielding copolymers with oligoaniline side chains. The properties of these copolymers, such as organic solubility, thermal stability, electroactivity, electrical conductivity, dielectric properties and electrochromic performance are also described in detail.

EXPERIMENTAL

Materials

2,6-difluorobenzoyl chloride and *N*-phenyl-*p*-phenylenediamine were purchased from Aldrich. 4,4'-dichlorodiphenyl sulfone and 4,4'-isopropylidene diphenol were purchased from Shanghai Chemical Factory. K₂CO₃ was dried at 110 °C for 24 h before used. All other reagents were obtained from commercial sources and used as received without further purification. Distilled and deionized water was used. Optically transparent indium-tin oxide (ITO) glass substrates (Reintech electronic technologies, Beijing) with dimensions of 4.0 cm \times 0.6 cm \times 0.07 cm were used for electrochromic thin films electrode.

Synthesis of Parent Aniline Tetramer (PAT)

The parent aniline tetramer in emeraldine state was synthesized by oxidative coupling of *N*-phenyl-*p*-phenylenediamine in the presence of ferric chloride hexahydrate as an oxidant according to the method of Zhang et al.³⁶ The obtained PAT (5.0 g) was dispersed into a stirring mixture solution (30 mL of hydrazine hydrate in 400 mL of 1.0 M ammonium hydroxide) and stirred for 12 h. Then it was filtered and washed with distilled water for several times, followed by drying in vacuum. Finally, the PAT was reduced to the leucoemeraldine oxidation state. Yield: 94%. MALDI-TOF-MS: m/z calculated for $C_{24}H_{22}N_4 = 366.5$. Found 366.6.

FTIR (KBr, cm⁻¹): 3390 (s, $v_{\rm NH}$), 3020 (m, $v_{\rm CH}$), 1600 and 1527 (s, $v_{\rm C=C}$ of benzenoid rings), 1305 (s, $v_{\rm C-N}$), 815 (m, $\delta_{\rm CH}$), 746 (m, $\delta_{\rm CH}$), 692 (m, $\delta_{\rm CH}$). ¹H NMR (d₆-DMSO): δ = 7.78 (s, 1H, due to H₄), δ = 7.68 (s, 1H, due to H₃), δ = 7.43 (s, 1H, due to H₂), δ = 7.12 (t, 2H, due to H₆), δ = 6.87 (m, 12H, due to H₈), δ = 6.65 (t, 1H, due to H₅), δ = 6.51(d, 2H, due to H₇), δ = 4.62 (s, 2H, due to H₁).

Synthesis of DFAT

A solution of 5.28 g (30 mmol) 2,6-difluorobenzoyl chloride in 120 mL of dry methylene chloride was added dropwise over a period of 5 h to a stirring mixture of PAT (11.35 g, 31 mmol) and triethylamine (12 mL) in 300 mL of methylene chloride. The reaction, carried out in an atmosphere of dry nitrogen to avoid oxidation of PAT, proceeded readily at room temperature, with the formation of a grey solution. Following the addition of the solution of 2,6-difluorobenzoyl chloride, the resulting mixture was stirred for 1 h. The product, filtered from the mixture, was subsequently washed with methylene chloride two times, filtered and dried under dynamic vacuum at 45 °C for 24 h. The grey powder was obtained in 85% yield. MALDI-TOF-MS: m/z calculated for $C_{31}H_{24}F_2N_4O = 506.5$. Found 506.6.

FTIR (KBr, cm⁻¹): 3369 (s, $v_{\rm NH}$), 3299 (s, $v_{\rm NH}$), 1657 (vs, $v_{\rm C=0}$), 1600(s, $v_{\rm C=C}$ of benzenoid rings), 1525 (vs, $v_{\rm C=C}$ of benzenoid rings), 1303 (s, $v_{\rm C-N}$), 1008(m, $\delta_{\rm CF}$), 817 (m, $\delta_{\rm CH}$), 746 (m, $\delta_{\rm CH}$), 692 (m, $\delta_{\rm CH}$). ¹H NMR (d₆-DMSO): δ = 10.51 (s, 1H, due to H₁), δ = 7.80 (s, 1H, due to H₄), δ = 7.77 (s, 1H, due to H₃), δ = 7.48 (d, 2H, due to H₂), δ = 7.23 (t, 2H, due to H₆), δ = 7.14 (t, 2H, due to H₈), δ = 6.96 (m, 12H, due to H₁₀), δ = 6.68(t, 1H, due to H₅).

Synthesis of Electroactive Poly(arylene ether sulfone) Copolymers (PES-S-AT)

A typical synthesis procedure of PES-S-AT-40, where 40 refers to the feed percent of DFAT, was as follows. A mixture of DMAc (30 mL), toluene (10 mL), anhydrous potassium carbonate (1.423 g), DFAT (2.026 g, 4 mmol), 4,4'-dichlorodiphenyl sulfone (1.723 g, 6 mmol), and 4,4'-isopropylidene diphenol (2.283 g, 10 mmol) were added to a 100 mL three-necked round-bottom flask and heated to reflux under nitrogen with magnetic stirring for 2 h to remove the water by azeotropic distillation with toluene, and then the toluene was removed. The mixture was heated to reflux for 8 h to ensure the completion of the reaction. The solution was cooled to room temperature and poured into 400 mL water, which yielded a grey precipitate. The precipitate was washed with water and ethanol several times, filtered and dried under dynamic vacuum at 45 °C for 48 h Yield: 90%.

Preparation of the Poly(arylene ether sulfone) Copolymers in Emeraldine State Doped with HCl

The obtained polymers (0.5 g) was dispersed into a stirring mixture solution (ammonium persulfate in 30 mL of 1.0 M HCl) and stirred for 5 h. The mol quantity of ammonium persulfate corresponds to that of each PES-S-AT-x. Then the mixture was filtered using a Buchner funnel and water aspirator, and the filter cake was washed with distilled water for several times, followed by drying under dynamic vacuum at 50 °C for 24 h. Finally, the doped copolymers were proved in the emeraldine oxidation state by UV-Vis spectra.

Fabrication of Electrochromic Electrodes

The ITO substrates were cleaned ultrasonically in the ethanol for 5 min and in the deionized water for another 3 min. Then the ITO substrates dried in the air. Take PES-S-AT-100 copolymer as an example: the polymer (0.03 g) was dissolved in DMAc (1 mL) to form a blue solution, and filtered through 0.2- μ m poly(tetrafluoroethylene) syringe filter. Then the copolymer films were spin-coated onto the ITO substrates by the DMAc solution of PES-S-AT-100. The spin-coating process was firstly 500 rpm for 5 s and then 1000 rpm for 30 s. Before electrochromic measurements, a copper tape (1.0 cm \times 0.5 cm) was applied to the top edge of ITO substrates as the bus bar.

Measurement

Mass spectroscopy (MS) was performed on an AXIMA-CFR laser desorption ionization flying time spectrometer (COM-PACT). Fourier-transform infrared spectra (FTIR) measurements were recorded on a BRUKER VECTOR 22 Spectrometer by averaging 128 scans at a solution of 4 cm^{-1} in the range of 4000-400 cm⁻¹. The nuclear magnetic resonance spectra (NMR) of PAT, DFAT and PES-S-AT in deuterated dimethyl sulfoxide (DMSO) were run on a BRUKER-500 spectrometer to determine the chemical structure and tetramethylsilane was used as the internal standard. The number-average molecular weight (M_n) , weight-average molecular weight (M_w) , and molecular weight distribution of PES-S-AT were measured with a gel permeation chromatography (GPC) instrument equipped with a Shimadzu GPC-802D gel column and SPD-M10AVP detector with N,N' -dimethylformamide as an eluent at a flow rate of 1 mL min⁻¹. Calibration was accomplished with monodispersed polystyrene (PS) standards. Inherent viscosity was determined on an Ubbelohde viscometer in thermostatic container with the polymer concentration of 0.5 g/dL in NMP at 25 °C. The composition of PES-S-AT copolymer were calculated from the results of elemental analysis. The weight percentages of carbon, hydrogen, nitrogen and sulfur in the samples were measured by a Flash Ea 1112 elemental analysis instrument.

Spectrascopic Properties

UV-vis spectra were performed on UV-2501 PC Spectrometer (SHIMADZU) in DMF. Initial solution of PES-S-AT in the lecoemeraldine oxidation state was quite dilute (around 0.05 mg mL⁻¹).

Thermal Properties

Differential scanning calorimeter (DSC) measurements were performed on a Mettler Toledo DSC821^e instrument at a heating rate of 10 °C/min from 50 to 300 °C under nitrogen. The glass-transition temperatures (T_g) of the copolymers were reported as the midpoint of the step transition in the second heating run. A Perkin-Elmer PYRIS 1 TGA was used to investigate the thermal stability of the copolymers in the temperature range from 100 to 700 °C at a rate of 10.0 °C min⁻¹ under nitrogen protection.

Electrochemical Activity

The cyclic voltammetry (CV) was performed with a CHI 660A Electrochemical Workstation (CH Instruments) in a conventional three-electrode cell, by using thin films cast from DMAc solutions onto a g-c electrode. The film was cycled at 1.0 M $\rm H_2SO_4$ aqueous solution in the range from -100 mV to +1000 mV.

Electrochromic Performance

The electrochromic electrodes coated by PES-S-AT were applied a constant potential of 0, 0.2, 0.4, 0.5, 0.6, 0.8, and 1.0 V versus Ag/AgCl in the 0.5 M H_2SO_4 for 400 s. Then the electrochromic electrodes were rinsed with deionized water and dried by N_2 blewing. Subsequently, the change of color and transmittance were monitored with a digital camera (Canon, IXUS130) and UV-2501 PC Spectrometer (SHIMADZU).

Electric and Dielectric Properties

The electrical conductivity of the copolymers at room temperature (RT) was measured by a four-probe method using a 2182 Nanovoltmeter and 2400 Sourcemeter as the current source. Three samples of each copolymer were tested and the conductivity of each sample was measured four times at different current values. The average of 12 measurements was taken as the conductivity of the copolymer. The formula used for calculating conductivity is as follows: $\sigma = \frac{I \times 24.4}{U \times d \times h}$. Where σ , *I*, *V*, *d*, and *h* are conductivity (S cm⁻¹), current (A) set, voltage (V) measured, the width (mm) and thickness (mm) of the sample.

Dielectric spectroscopy was performed using a QuadTech 1920 LCR meter. Measurements of the capacitance(C) over the range of 0.1 kHz to 1 MHz were carried out with the pressure compressed circular pellets of the pristine material, ~1 cm in diameter with a thickness of 0.4 mm. The dielectric constant (ε') were calculated from capacitance using the following equation: $\varepsilon' = \frac{4Cd}{\pi D^2 E_0}$, where d is the thickness and D is the diameter of the sample, and E_0 , the permittivity of the free space, is 8.854 × 10⁻¹² F/m.

RESULTS AND DISCUSSION

Synthesis and Characterization of Monomers

The synthetic route of PAT and DFAT is outlined in Scheme 1. According to a well-established synthetic method,³⁰ PAT was successfully synthesized by oxidative coupling of *N*-phe-nyl-*p*-phenylenediamine using ferric chloride hexahydrate as an oxidant, followed by reduction using hydrazine hydrate in 1.0 M ammonium hydroxide. DFAT was prepared by the



SCHEME 1 Synthesis of parent aniline tetramer (PAT) and 2,6-difluorobenzoyl aniline tetramer (DFAT).

reaction between 2,6-difluorobenzoyl chloride and PAT in the presence of triethylamine at a yield of 85%. The synthesized PAT and DFAT were fully characterized by MALDI-TOF spectra, FTIR, and ¹H NMR spectroscopy. Figure 1 illustrates the ¹H NMR spectra of PAT and DFAT in DMSO-d₆. The¹H NMR spectra clearly reveal that the primary aromatic amino groups (NH₂) have been completely transformed into acylamino groups (—CO—NH—) by the low-field shift of the proton H₁ and H₇. The relative intensities and expected splitting of the aromatic proton signal is also seen, demonstrating the well-defined structure of PAT and DFAT.

Synthesis and Characterization PES-S-AT Copolymers

The synthetic routes for preparation of poly(arylene ether sulfone) copolymers with pendant oligoaniline groups are depicted in Scheme 2. All the polymerizations proceeded homogeneously by K_2CO_3 -mediated nucleophilic aromatic polymercondensation using 4,4'-isopropylidene diphenol as bisphenol monomer. Copolymers with different pendants ratio could be obtained by adjusting the feed of DFAT to 4,4'-dichlorodiphenyl sulfone. The reaction temperature was first controlled at 140 °C to remove the water by azeotropic distillation with toluene, and then increased to 163 °C to accomplish polymerization.

The chemical structures of PES-S-AT copolymers were confirmed by FTIR, ¹H NMR spectroscopy and GPC. FTIR spectra of PES-S-AT copolymers (Fig. 2) showed the characteristic absorption bonds around 3394 cm⁻¹ corresponding to N-H stretching vibration, around 2930 cm⁻¹ based on C-H stretching vibration of methyl groups and around 1650 cm⁻¹ due to C=0 stretching vibration in aryl carbonyl groups. The vibration at around 1600 cm^{-1} and 1504 cm^{-1} is attributed to the stretching vibration of C=C in the benzene rings, and the peak at 1235 cm^{-1} can be assigned to the stretching vibration of C-O-C of the aryl ether linkages. The bands at 1454 cm⁻¹($v_{C=C}$), 1294 cm⁻¹(v_{C-N}), 1049 cm⁻¹(δ_{CH}), and 748 cm⁻¹(δ_{CH}), based on the structure of oligoaniline, were found to increase as the concentration of oligoaniline in the polymer increased. And the bands at 1149 cm⁻¹($v_{0=S=0}$), 1105 cm⁻¹(δ_{CH}), and 559 cm⁻¹(δ_{CH}), attributed to the vibration of diphenylsulfone segments, decrease as the concentration of oligoaniline in the polymer increased. The ¹H NMR spectra of PES-S-AT copolymers are shown in Figure 3. The signals at $\delta = 10.24$, 7.73, 7.67, 7.59 ppm are attributed to the amino protons and the signals around δ = 1.68–1.50 ppm are ascribed to the methyl protons. Aromatic protons

adjacent to the sulfone groups (H₁₁) appeared at high frequency area (around 7.86 ppm) because of the strong electron-drawing effects. Furthermore, the signal of H₈ exhibits triplet at 7.14 ppm in the ¹H NMR spectrum of DFAT, but it appears doublet at 6.66 ppm in the ¹H NMR spectrum of PES-S-AT copolymers, which confirms that the fluorine groups have been completely reacted to the hydroxyl groups during the nucleophilic polymercondensation reaction. The integral area ratio of H_{11} to H_{15} , obtained from the ¹H NMR spectrum, are given in Table 1. Then the value of x in the PES-S-AT-x are 19.6, 38.8, 58.0, 78.7, and 100, deduced from the integral area ratio of H₁₁ to H₁₅. Typical elemental analysis for PES-S-AT-x are shown in Table 1, as are the ratio of Sulfur to Nitrogen. The data of ¹H NMR and elemental analysis verifies that the PES-S-AT copolymers have been synthesized according to expectation, which indicate that the DFAT has the similar reaction activity to 4,4'-dichlorodiphenyl sulfone in K₂CO₃-mediated nucleophilic aromatic polymercondensation reaction. The number average molecular weight $(M_{\rm n})$ and the polydispersity index of the copolymers, obtained by GPC, are presented in Table 2.



FIGURE 1 ¹H NMR spectra of PAT and DFAT.



SCHEME 2 Synthesis of PAE-S-AT-x copolymers. (x represents the oligo-anilines mole percent of the copolymers).

These copolymers were obtained in almost quantitative yields, with inherent viscosities in the range of 0.12–0.18 dL/g, as shown in Table 2. It is too low compared with that of ordinary polymers, because the bulky pendant groups in chemical structure impede the interchain entanglement to some extent. The PES-S-AT copolymers exhibited outstanding solubility in polar solvents such as THF, NMP, DMAc, DMF and DMSO (Table 3). During the solubility test, an interesting phenomenon was found: the copolymers with high ratio of





FIGURE 3 ¹H NMR spectra of PAE-S-AT copolymers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Polymer	C (wt %)	H (wt %)	N (wt %)	S (wt %)	n <u>s</u> N	nsal N	$R_{{\rm H_{11}}\over{\rm H_{15}}}$	X^{exp}	X^{cal}
PAE-S-AT-20	75.08	5.12	2.20	5.24	1.041	1.000	0.536	19.6	20.0
PAE-S-AT-40	76.52	5.25	4.09	3.56	0.380	0.375	0.408	38.8	40.0
PAE-S-AT-60	77.70	5.33	5.64	2.19	0.170	0.166	0.280	58.0	60.0
PAE-S-AT-80	78.72	5.41	6.93	1.02	0.064	0.063	0.142	78.7	80.0
PAE-S-AT-100	79.54	5.51	8.03	0.00	0.000	0.000	0.000	100.0	100.0

TABLE 1 The Elemental Analysis and ¹H NMR Data of the PAE-S-AT Copolymers

 $n_{\frac{N}{N}}$, molar ratio of sulfur to nitrogen; $R_{\frac{H_{11}}{N}}$, integral area ratio of H_{11} to H_{15} from the ¹H NMR spectra; X, the amount of oligoaniline side groups; exp, experimental data; cal, calculated data.^{H_{15}}

pendants (such as PES-S-AT-100, PES-S-AT-80) possess excellent solubility in acetone, while the copolymers with low ratio of pendants (such as PES-S-AT-20, PES-S-AT-40) possess good solubility in the solvent of methylene chloride and chloroform. The exciting solubility of PES-S-AT copolymers in the common organic solvent makes this an attractive system for both academic research and industrial applications.

Thermal Properties

The thermal properties of PES-S-AT copolymers were evaluated by their Tg and Td data (Table 2) measured by DSC and TGA, respectively. The Tg of the PES-S-AT copolymers decreased from 166 °C to 150 °C as the concentration of pendants in the polymer increased, which attribute to the bulky pendant groups in chemical structure hindering interchain interaction. The thermal stability of the synthesized PES-S-AT copolymers was studied under identical drying and heating conditions. The typical TGA curves are shown in Figure 4. The process of loss weight undergoes only one step beginning at 300 °C for the decomposition of main chain. Table 2 gave the 5 and 10% weight loss temperatures of the obtained copolymers. It indicates that the PES-S-AT copolymers have good thermal resistance compared with usual PANI materials.³⁷ Moreover, the copolymers with low ratio of pendants (such as PES-S-AT-20, PES-S-AT-40) possess better thermal stability, because the oligoaniline segment is not as stable as the other aromatic segment under high temperature, and is liable to decompose first. The results demonstrate that the PES-S-AT copolymers had good thermal stability and higher degradation temperature.

Spectroscopic Properties

Take PES-S-AT-100 copolymer as an example: a sample was dissolved in DMAc solution followed by the addition of trace amount of $(NH_4)_2S_2O_8$. The solution gradually turned to dark blue and finally purple upon being oxidized. This process was monitored by UV-vis spectra with time intervals about 4 mins; the obtained UV-vis spectra are presented in Figure 5. First, two absorption peaks at 287 nm and 330 nm were observed, which are associated with $\pi - \pi^*$ transition transitions in the benzoid rings. When slow oxidation took place, the absorption peak at 330 nm started to undergo a blue shift (from 330 nm to 306 nm) while decreasing in intensity, and the UV-vis spectra showed a new absorption peak at about 570 nm. This is assigned to exciton-type transition between the HOMO orbital of the benzoid ring and the LUMO orbital of the quinoid ring and continually increased in intensity. When its intensity reached the maximum, the PAE-S-AT copolymer was in the emeraldine oxidation state with parent aniline tetramer segment containing one quinoid rings (Scheme 3). With further oxidization of PES-S-AT copolymer, all the absorption peaks decreased and the absorption peak at 570 nm began to undergo a red shift to 655 nm. Finally the absorption in the range of 400 nm and

TABLE 2 T	The I	Basic	Properties	of the	PAE-S-AT	Copol	ymers
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Polymer	η ^a (dL/g)	Т _g ь (°С)	<i>T</i> d5 ^c (°C)	<i>T</i> _{d10} ^d (°C)	$M_{\rm n}^{\rm e}$	$M_{\rm w}/M_{\rm n}$	σ ^f (S/cm)
PAE-S-AT-20	0.18	166	438	459	29,300	2.57	5.96×10^{-7}
PAE-S-AT-40	0.15	159	410	436	10,300	3.06	$1.12 imes 10^{-6}$
PAE-S-AT-60	0.15	156	400	433	37,400	2.33	$4.73 imes 10^{-6}$
PAE-S-AT-80	0.15	152	404	432	13,700	1.86	8.27×10^{-6}
PAE-S-AT-100	0.12	150	377	417	9,600	1.47	$2.36 imes 10^{-5}$

 a Inherent viscosity was determined on an Ubbelohde viscometer in thermostatic container with the polymer concentration of 0.5 g/dL in NMP at 25 $^\circ$ C.

^b Glass transition temperature by DSC.

^c 5% Weight-loss temperatures were detected at a heating rate of 10 °C/min, in nitrogen.

^d 10% Weight-losses temperatures were detected at a heating rate of 10 °C/min in nitrogen.

^e The number-average molecular weight and molecular weight distribution were measured with a gel permeation chromatography with DMF as an eluent at a flow rate of 1 mL/min.

^f The electric conductivity of the copolymers doped with HCl in emeraldine oxidation state was measured by a four-probe method.

	Acetonitrile	CH_2CI_2	CHCI ₃	Acetone	THF	DMF	DMA
PAE-S-AT-20	_	+	+	_	+	+	+
PAE-S-AT-40	_	+-	+	-	+	+	+
PAE-S-AT-60	_	_	+-	+-	+	+	+
PAE-S-AT-80	_	-	_	+	+	+	+
PAE-S-AT-100	_	_	_	+	+	+	+

TABLE 3 The Solubility of the PAE-S-AT Copolymers in the Different Solvents

The solubility of the PAE-S-AT-X was determined with 5% solid content at 25 $^{\circ}$ C; +, soluble; +-, partially soluble; -, insoluble.

800 nm disappeared, which showed that the PES-S-AT copolymer has reached in the pernigraniline oxidation state. The chemical oxidation process of PES-S-AT-100 copolymer is similar to that of polymer bearing oligoaniline groups. However, the absorption peak at 570 nm of PES-S-AT copolymers undergoes a red shift when it transform from emeraldine oxidation state to pernigraniline oxidation state, which is contrast to that of polyaniline, oligoaniline and oligoaniline-containing polymers.^{30,38,39} The phenomenon indicates that the bandgap between the HOMO and LUMO of the polymers should decrease when it transform from emeraldine oxidation state to pernigraniline oxidation state, which would be caused by the unique chemical structure. Further studies in the regard are currently underway.

Electrochemical Activity

Figure 6 shows the cyclic voltammetry of the synthesized PES-S-AT-(100, 80, 60, 40, 20) copolymers and DFAT obtained in 1.0 M H_2SO_4 aqueous solution using Ag/Ag⁺ as the reference electrode with a scan rate of 100 mV s⁻¹. A THF solution of PES-S-AT copolymers and DFAT was cast on the g-c working electrode and was evaporated to form a thin solid film. Under these conditions, the cyclic voltammetry of DFAT shows two pairs of redox peaks with oxidation peaks at 320, and 520 mV, respectively. It indicated that DFAT possess three oxidation states, that is, Leucoemeraldine, Emeraldine, and Pernigraniline (Scheme 3), which is similar to polyaniline.²⁶ The films of the PES-S-AT copolymers on the g-c

FIGURE 4 TGA thermograms of the PAE-S-AT copolymers in $N_{\rm 2}.$

working electrode, prepared using the identical volume with the same concentration, were used to evaluate the electroactivity. In the cyclic voltammetry of the PES-S-AT copolymers, two pairs of redox peaks appear with oxidation peaks at 330 and 530 mV in that of PES-S-AT-100 and PES-S-AT-80, which are shift slightly compared with DFAT due to the difference of molecular structure. But in the cyclic voltammetry of PES-S-AT-(60, 40, 20), only one pair of redox peaks appear with oxidation peaks around 530 mV, owing to the weak electroactivity caused by the lower concentration of oligoaniline. In addition, the maximum current value of each copolymer was found to increase as the pendant concentration in the polymer increased.

Electrical and Dielectric Properties

Electrical conductivity of the doped copolymers in emeraldine oxidative state at room temperature are between 2.36 $\times 10^{-5}$ and 5.96 $\times 10^{-7}$ S cm⁻¹and increase as the concentration of oligoaniline in the polymer increased. However, the conductivity of the obtained copolymers are much lower than that for the HCl-doped polyaniline (1.0 S cm⁻¹) and parent aniline tetramer (3.0 $\times 10^{-3}$ S cm⁻¹). This is attributed to the rigidity of the backbone precluding aggregation of the aniline tetramers into a continuous conducting region.

Recently, we have prepared a kind of high dielectric constant material using polymers with oligoaniline in the main chain,^{40,41} which would solves phase separation, migration, and extraction problems existing in traditional high dielectric constant PANI/polymer blends.^{42–44} Although dielectric properties of polymers with oligoaniline in the main chain were well documented, the dielectric properties of polymers with oligoaniline as the pendants have been rarely reported.

Measurements of the dielectric response over the range of 0.1 kHz to 1 MHz were carried out with pressure compressed pellets of polymers; then gold electrodes were sputtered on the two surfaces of the pellets to form electrodes. Figure 7 demonstrates the variation of dielectric constant with frequency for pristine PES-S-AT copolymers, and doped PES-S-AT copolymers in the emeraldine oxidative state (HCl-treated) at room temperature. In the insert graph of Figure 7, it reveals that pristine PES-S-AT copolymers gave ε' values around 3.3 detected at a frequency of 0.1 kHz, and then decreased to 2.5 as the frequency was increased to 1 MHz, respectively. The diagram illustrates that pristine PES-S-AT copolymers possess dielectric constant corresponding to that

FIGURE 5 UV–vis spectra monitoring the chemical oxidation of the PAE-S-AT-100 with time intervals about 4 mins. (a): from the leucoemeraldine oxidation state to the emeraldine oxidation state; (b): from the emeraldine oxidation state to the pernigrailine oxidation state. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

of traditional polymers. After doping with HCl, the PES-S-AT copolymers in the emeraldine oxidative state have enhanced dielectric constants at frequency between 0.1 kHz and 1 MHz. Such as, PES-S-AT-100 copolymer possesses ε' values of 78.05, 11.96, and 5.49 at frequencies of 0.1 kHz, 10 kHz, and 1 MHz, respectively. And it displays the dielectric constant of the copolymers decreased significantly with the increase of frequency. The phenomena and mechanism of this dielectric behavior is similar to that of electroactive polymers as previously reported.^{40,41} Moreover, the dielectric constants of PES-S-AT copolymers were found to decrease as the pendant concentration in the polymer decreased.

Electrochromic Studies

It is well established that the ability of a polymer to exhibit a rapid color change in different redox states is important for the electrochromic applications. Among various electrochromic polymers, polyaniline is particularly attractive due to its unique optical properties and high environmental stability.^{45,46} In addition, the transformation of oxidation states is highly repetitive under low driving potential, and its color contrast is high in the visible light region. It was envisioned that the oxidation states transformation and color change would likewise occur at the oligoaniline linkages of polymers; hence, the PES-S-AT copolymers were subsequently analyzed for their abilities to exhibit electrochromic characteristics.

Spectroelectrochemical measurements were performed on PES-S-AT-100 copolymer by increasing the potential from 0.0 to 1.0 V and in conjunction with the acquisition of UV-vis spectral data. The typical electrochromic photographs are shown in Figure 8. The material underwent a drastic color change from grey (at 0.0 V), to green (at 0.4 V), to blue (at 0.6 V) and to pearl blue (at 1.0 V) during the oxidation process. The transmittance spectra in Figure 9 shows that the ITO electrochromic performance. The maximum transmittance change (ΔT) at 700 nm is 42.6% [90.7% (at 0.0 V) \leftrightarrow 48.1% (at 0.6 V)]. Moreover, the copolymer thin films exhibit stronger adherence to the ITO glass substrates and better repetition of redox behaviors than polyaniline. Although similar results were obtained for other copolymers (PES-S-

SCHEME 3 Molecular structures of DFAT at various oxidation states.

FIGURE 6 Cyclic voltammograms of the PAE-S-AT copolymers with a scan rate of 100 mV s⁻¹ (insert: cyclic voltammetry of DFAT with a scan rate of 100 mV s⁻¹). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

FIGURE 7 Frequency dependence of dielectric constant of PAE-S-AT copolymers in pristine form and emeraldine oxidation state with HCI-doped form, respectively. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary. com.]

AT-20, -40, -60, -80), only slight color change and maximum transmittance change (ΔT) (700 nm) were observed, which is in accord with the decreased percentage of oligoanilines.

CONCLUSIONS

We have synthesized a series of novel copolymers of poly (arylene ether sulfone) with oligoaniline groups as pendants by nucleophilic polymercondensation reaction. The synthesized copolymers PES-S-AT exhibit a broad and strong absorption in visible region, good solubility in the organic solvents and excellent thermal stability. Furthermore, the electroactivity, electric and dielectric properties of the PES-S-AT copolymers were investigated in detail. Preliminary studies on electrochromic properties of PES-S-AT copolymers afforded the electrochromic electrode with an obvious color change and maximum transmittance change of 42.6%. Given

FIGURE 8 Photographs of PES-S-AT-100/ITO electrodes in 0.5 M H_2SO_4 at different potentials (vs. Ag/AgCl) for 400 s.

FIGURE 9 Optical transmittance of PES-S-AT-100/ITO electrodes in 0.5 M H_2SO_4 at different potentials (vs. Ag/AgCI) for 400 s. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the good solubility, processability, electroactivity, thermal stability, dielectric and electrochromic properties, the PES-S-AT copolymers have great potential for foreseen applications, such as antistatic coatings, wave-absorbing materials, electrochromic devices, and thin films in electronic applications, etc.

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