Supporting Information

Linkage Effect on Memory Behavior of Sulfonyl-containing Aromatic Polyether, Polyester, Polyamide, and Polyimide

By Chih-Jung Chen, Yi-Cheng Hu, and Guey-Sheng Liou*

Functional Polymeric Materials Laboratory, Institute of Polymer Science and Engineering, National Taiwan University, Taipei, Taiwan Tel: +886-2-3366-5315; Fax: +886-2-3366-5237; E-mail: <u>gsliou@ntu.edu.tw</u>

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Polymer Synthesis

Synthesis methods of **DSPE**

A three necked 50 ml glass reactor was charged with diol monomer 4,4'-dihydroxyltriphenyamine (0.14 g, 0.5 mmol), 4,4'-difluorodiphenyl sulfone (0.13 g, 0.5 mmol), 1.5 ml *N*-methyl-2-pyrrolidinone (NMP), 1 ml of toluene, and potassium carbonate (0.15 g, 0.75 mmol). The reaction mixture was heated at 150 °C for 3 h to remove water during the formation of phenoxide anions, and then heated at 170 °C for 1 h, 180 °C for 3 h, and finally heated at 190 °C for 1 h. After the reaction, the obtained polymer solution was poured slowly into 300 ml of acidified methanol/water (v/v = 1/1). The precipitate was collected by filtration, washed thoroughly with hot water and methanol, and dried under vacuum at 100 °C.

Synthesis methods of DSPET

A mixture of 0.15 g (0.53 mmol) diol monomer 4,4'-dihydroxyltriphenyamine, 0.18 g (0.53 mmol) 4,4'-sulfonyldibenzoyl chloride, and 1.5 mL of *o*-dichlorobenzene was heated with stirring at 180°C for 15 h under nitrogen. The solution thus obtained was poured into 300 mL of methanol. The yield of the polymer was 0.29 g (98%), and the inherent viscosity was 0.27 dL/g in dimethylacetamide (DMAc). The IR spectrum (film) showed an absorption at 1737 cm⁻¹ (C = O).

Synthesis methods of DSPA

A mixture of 0.28 g (1.0 mmol) of 4,4'-diaminotriphenylamine, 0.31 g (1.0 mmol) of 4,4'-sulfonyldibenzoic acid, 0.1 g of calcium chloride, 1.0 mL of triphenyl phosphite (TPP), 0.5 mL of pyridine, and 1.0 mL of NMP was heated with stirring at 105 °C for 3 h. The polymer solution was poured slowly into 300 mL of stirring methanol giving rise to a stringy, fiber-like precipitate that was collected by filtration, washed thoroughly with hot water and methanol successively, and dried under vacuum at 100 °C. Reprecipitation from DMAc into methanol was carried out twice for further purification.

Synthesis methods of **DSPI**

To a solution of 1.0 mmol of 4,4'-diaminotriphenylamine in 2.8 mL of NMP, 0.45 g (1.01 mmol) of 3,3',4,4'-diphenylsulfonetetracarboxylic dianhydride was added in one portion. The mixture was stirred at room temperature overnight (ca. 12 h) to afford a viscous poly(amic acid) solution. The poly(amic acid) was subsequently converted to polyimide via a chemical

imidization process by addition of pyridine 1.0 mL and acetic anhydride 2.0 mL, then the mixture was heated at 120 °C for 4 h to complete imidization. The resulting polymer solution was poured into 300 mL of methanol giving a fibrous precipitate washed thoroughly with methanol.

Polymer Properties Measurements

Fourier transform infrared (FT-IR) spectra were recorded on a PerkinElmer Spectrum 100 Model FT-IR spectrometer. The inherent viscosities were determined at 0.5 g/dL concentration using Tamson TV-2000 viscometer at 30 °C. Gel permeation chromatographic (GPC) analysis was carried out on a Waters chromatography unit interfaced with a Waters 2410 refractive index detector. Two Waters 5 µm Styragel HR-2 and HR-4 columns (7.8 mm I. $D. \times 300 \text{ mm}$) were connected in series with NMP as the eluent at a flow rate of 0.5 mL/min at 40 °C and were calibrated with polystyrene standards. Thermogravimetric analysis (TGA) was conducted with TA SDT Q600. Experiments were carried out on approximately 6-8 mg film samples heated in flowing nitrogen or air (flow rate = $20 \text{ cm}^3/\text{min}$) at a heating rate of 20 ^oC/min. DSC analyses were performed on a PerkinElmer Pyris 1 DSC at a scan rate of 10 °C/min in flowing nitrogen (20 cm³/min). Electrochemistry was performed with a CH Instruments 611B electrochemical analyzer. Voltammograms were presented with the positive potential pointing to the left and with increasing anodic currents pointing downwards. Cyclic voltammetry (CV) was conducted with a three-electrode cell in which ITO (polymer films area about 0.5 cm x 1.1 cm) was used as a working electrode. A platinum wire was used as an auxiliary electrode. All cell potentials were taken by using a homemade Ag/AgCl, KCl (sat.) reference electrode. UV-visible absorption was recorded on UV-visible spectrophotometer (Hitachi U-4100).

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Figure S1. Synthesis methods of DSPE, DSPET, DSPA, and DPSI.



Figure S2. IR spectrum of DSPET.



Figure S3. TGA thermograms and DSC traces of DSPET.



Figure S4. UV-visable absorption spectra of sulfonyl-containing polymers.



Figure S5. Cyclic voltammetric diagrams of polymer films on an ITO-coated glass substrate over cyclic scans.



Figure S6. Simulation conformation of DSPE, DSPET, DSPA, and DSPI.

Polymer	$\eta_{\rm inh}^{a}$ (dL/g)	$M_w^{\ \ b}$	$M_n^{\ b}$	PDI^{c}
DSPE	0.29	65,000	25,000	2.60
DSPET	0.27	91,000	40,300	2.26
DSPA	0.35	61,700	34,500	1.79
DSPI	0.31	109,000	52,000	2.10

Table S1. Inherent Viscosity and Molecular Weights of Polymers

^{*a*} Measured at a polymer concentration of 0.5 g dL⁻¹ in DMAc at 30 °C.

^b Calibrated with polystyrene standards, using NMP as the eluent at a constant flow rate of 0.5 ml/min at 40 °C.

^{*c*} Polydispersity Index (M_w/M_n) .

Table S2.	Solubility	Behavior	of DSPET
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Code	Solubility in various Solvent ^a						
Coue -	NMP	DMAc	DMF	THF	CHCl ₃	DMSO	<i>m</i> -cresol
DSPET	++	++	+	++	++	+	+
0							

^{*a*} Qualitative solubility was tested with 10 mg of a sample in 1 mL of solvent. ++, soluble at room temperature; +, soluble on heating; -, insoluble even on heating.

Table S3. Thermal Properties of DSPET

Polymer ^a	T_{g}^{b} (°C)	$T_{\rm d}^{5} (^{\rm o}{\rm C})^{c}$		$T_{\rm d}{}^{10} ({}^{\rm o}{\rm C}){}^{c}$		$R_{ m w800}\left(\% ight)^{d}$
		N_2	Air	N_2	Air	
DSPET	208	455	435	480	460	55

^{*a*} The polymer film samples were heated at 250 °C for 1 h prior to all the thermal analyses.

^b Midpoint temperature of baseline shift on the second DSC heating trace (rate: 20 °C /min) of the sample after quenching from 400 °C to 50 °C (rate: 200 °C /min) in nitrogen

^c Temperature at which 5 % and 10% weight loss occurred, respectively, recorded by TGA at a heating rate of 20 °C/min and a gas flow rate of 20 cm³/min.

^dResidual weight percentages at 800 °C under nitrogen flow.