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

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Introduction

Bistable resistive switching polymeric materials[1] have been investigated for last three decades since the first polymer electronic memories reported by Sliva er al.[2] in 1970. According to our previous study[3] the differences of HOMO energy level, LUMOs charge density isosurfaces, dipole moment, and linkage conformation between polyimide and polyamide were found to affect the volatile memory behavior themselves. It is interesting to get more insight into the relationship between memory properties and linkage effect of functional polymers.[4] To the best of our knowledge, the memory properties of polyether and polyester have not been reported to date.

Results and Discussion

Chemical structures and preparation methods of these sulfonyl-containing polymers are illustrated in Scheme 1. UV-vis absorption spectra of these polymers are shown in Figure 1 and the onset wavelengths of optical absorption were utilized to obtain the optical energy band gap (E_g) of these polymers. The electrochemical behavior of these polymers was investigated by cyclic voltammetry conducted by film cast on an ITO-coated glass substrate as the working electrode in dry acetonitrile (CH_3CN) containing 0.1 M of TBAP as an electrolyte under nitrogen atmosphere. The typical cyclic voltammograms for these four polymers are depicted in Figure 2. The optical and electrochemical properties of these four polymers are summarized in Table 1. The LUMO energy levels of these polymer decrease with the electron-withdrawing ability of electron increasing, and are in the order of **DSPE**, **DSPET**, **DSPA**, and **DSPI**. The memory behaviors of these polymers were depicted by the current-voltage (I-V) characteristics of an ITO/polymer/Al sandwich device. The memory devices of **DSPE** did not possess the switch capability and retain at low-conductivity (OFF) state during the ambipolar scan, as shown in Figure 3 (a). Figure 3 (b) reveal I-V characteristics of **DSPA**. During the first negative sweep from 0 V to -6 V, the tremendous and sharp increased in current indicating the switch phenomenon could be observed at the threshold voltage of-3.2 V indicating the transition from the OFF state to high-conductivity (ON) state, defined as writing process. The device maintained at the ON state during the subsequent negative scan and then positive scan, defined as reading processing. The obtained ON state of these three devices could not erase by the reverse bias scan but relax to OFF state only if after stopping the electrical impulse for 8 minutes. The 8 minutes retention time at the ON state yet volatile, leading the static random access memory (SRAM) nature of this thin film while it were applied as the active layer in RRAM applications. Figure 3 (c) reveal I-V characteristics of **DSPI**. The device fabricated by **DSPI** showed the switch behavior at the threshold voltage of -4.0 V, the corresponding ON state could be read by conducting the negative and positive subsequently. The ON state would relax to OFF state without any erasing program but after removing the electric field for 4 min, and the device transited to ON state again at the switch-on voltage of -3.9 V, resulting as the SRAM behavior.

According to previous literatures[1], when the applied electric fields reach the switching-on voltage, some electrons at the HOMO accumulate energy and transit to the LUMO to form a charge transfer complex (ON state). Based on this mechanism, **DSPE** exhibit the insulator behavior due to the large band gap and weak charge transfer capability. **DSPA** have longer retention time than **DSPI** resulting from the conformation of phenyl ring with amide linkage is not a planar structure which may block the back CT occurring. The LUMO energy levels of **DSPET** locate between **DSPA** and **DSPI**, however, the no-planar linkage of polyester between donor and acceptor (isolated C-O bond) are expected to have longer retention time among all polymers.

Conclusions

Four sulfonyl-containing polymers were synthesized in this study. The relationship between memory properties and linkage effect of functional polymers was investigated and revealed interesting results. By choosing the suitable linkage between electron donor and acceptor, tunable memory properties (from insulator to different retention time SRAM) could be obtained.

Reference

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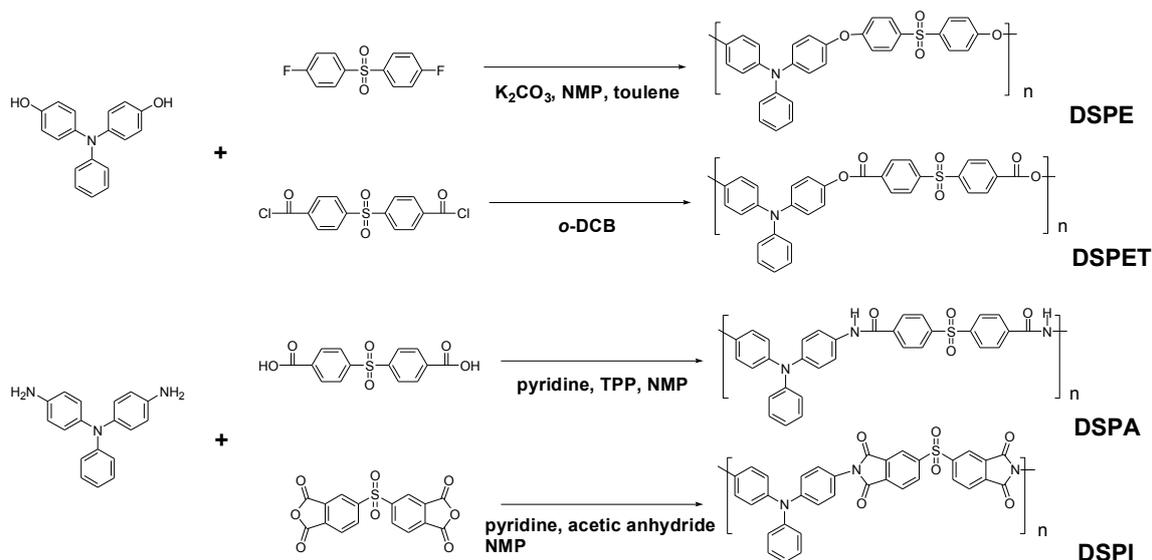
Scheme 1. Synthesis and structures of sulfonyl-containg polymers.

Table1. Redox Potentials and Energy Levels of Polymers

Polymer	Thin film (nm)	Oxidation potential (V)[a]		E_g (eV)[b]	HOMO (eV)[c]	LUMO^{opt} (eV)
	λ_{onset}	$E_{1/2}$	E_{onset}			
DSPE	361	0.93	0.68	3.43	5.12	1.69
DSPET	458	-	0.84	2.71	5.28	2.57
DSPA	496	0.87	0.74	2.50	5.18	2.68
DSPI	516	1.12	0.86	2.40	5.30	2.90

[a] From cyclic votammograms versus Ag/AgCl in CH_3CN. $E_{1/2}$: Average potential of the redox couple peaks.
[b] The data were calculated from polymer films by the equation: $E_g = 1240/\lambda_{onset}$ (energy gap between HOMO and LUMO).
[c] The HOMO energy levels were calculated from cyclic voltammetry and were referenced to ferrocene (4.8 eV; $E_{onset} = 0.36$ V).

LUMO^{Opt} (LUMO energy levels calculated from optical method): Difference between HOMO^{EC} and E_g^{Opt}.
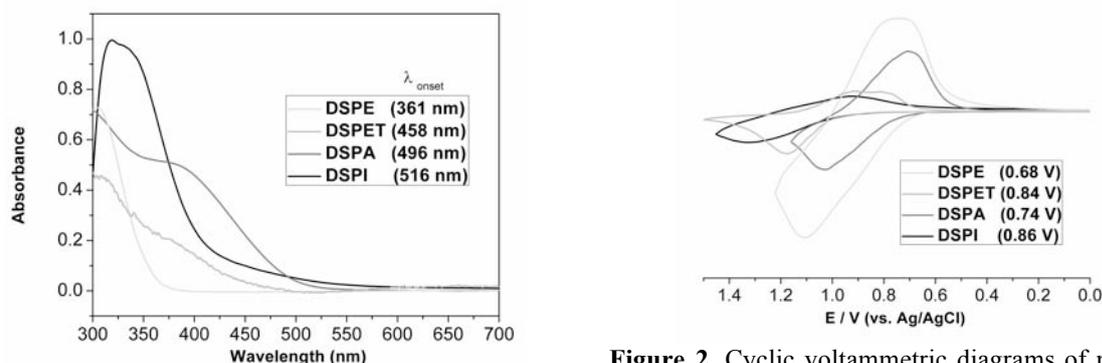
Figure 1. UV-visable absorption spectra of sulfonyl-containg polymers.

Figure 2. Cyclic voltammetric diagrams of polymer films on an ITO-coated glass substrate over cyclic scans.
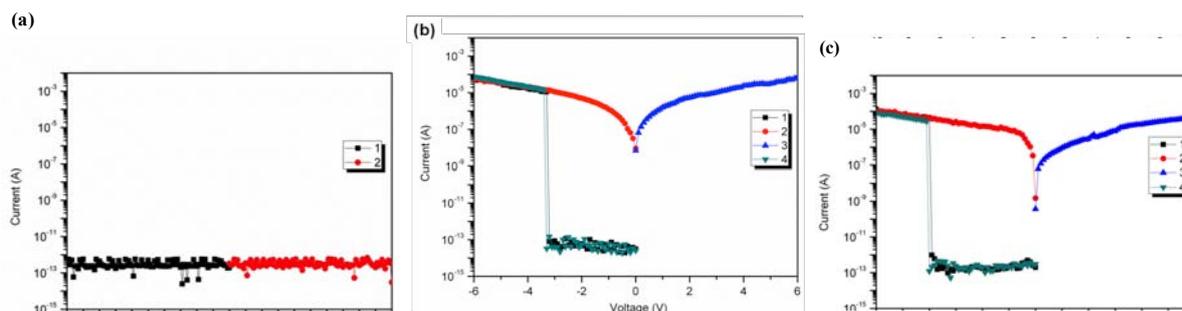
Figure 3. Current-voltage (I-V) characteristics of the ITO/polymer (50 ± 3 nm)/Al memory device. (a) **DSPE** (b) **DSPA** (c) **DSPI**.