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Chemical linkage functions of poly(ether imide)s on the resistive switching memory effects

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ABSTRACT

A series of aromatic poly(ether imide)s, **AZTA-PEI**s containing triphenylamine and 1,2,4-triazole moieties are prepared and characterized. All the polymers with inherent viscosity from 0.58 to 1.1 dL/g show glass transition temperatures in the range of 250–278 °C. Resistive switching memory devices are constructed based on the processable poly(ether imide) (**AZTA-PEIa**). The device can be switched from the initial OFF state to the ON state under either positive or negative electrical sweep at about ±3.2 V. The ON state is nonvolatile and can maintain the high conducting state even turning off the electrical power and applying a reverse bias. The device fulfills the requirements of a write-once read-many times memory (WORM) with a high ON/OFF current ratio up to 10^5 and a long retention time in both ON and OFF states. The bistable switching effects of the polymer result from the conformation-coupled charge transfer from electron donors (triazole-substituted triphenylamine moieties) to electron acceptors (phthalimide moieties). By comparing with the memory behaviors of analogue polymers, the functions of ether and imide in the chemical polymer structure on the memory behaviors are discussed.

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1. Introduction

Recently, resistive random access memory (RRAM) has attracted great attention due to its potential for the replacement of memory in next-generation memory applications [1,2]. Polymer electronic memories are potentially an alternative or a supplementary technology to the conventional memory technology facing challenges in miniaturizing from micro- to nano-scale [1,2]. Polymer memories can be processed at low cost and with their use the multi-stack layer structures required for highly dense memory devices can easily fabricated [3–6]. The approach of properties-tuning by combined molecular design and engineering, and materials synthesis and pro-

cessing, has allowed the simulation of various electronic memory effects and devices [7], including dynamic random access memory (DRAM), [8–11] flash (rewritable) memory, [12–18] write-one read-many-times (WORM) memory [19–23] and static random access memory (SRAM) [24–28]. With an understanding of the current state of memory technology and the basic concepts of electronic memories, the historical development of polymer electronic memories can be classified into three categories by drawing the mechanistic analog between the polymer memory element and one of the three primary circuit elements, *viz.*, capacitor, transistor and resistors.

Data storage in resistor-type memories is based on electrical bistability (ON- and OFF-states) arising from changes in intrinsic properties, such as charge transfer interaction, phase/conformation changes and changes in redox states, of the electro-active polymers in response to an applied electric field. A number of polymer materials, including conjugated polymers [29–31], polyimides [5,8,24,32–35],

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poly(aryl ether)s [12], and others [4,36,37] have been investigated for memory applications. Different kinds of memory devices have been discovered and the driving force behind these memory devices basically depends on many kinds of mechanisms such as "trapping–detrapping", and "charge transfer", and "conformational change" [1,2].

Kang and co-workers reported a flash memory effect of PVK modified with covalently bonded C_{60} [36] and developed PVK derivatives [37] with flexible spacers between the carbazole pendant groups and polymer backbone, for the conformation-induced WORM and volatile memory device applications, respectively. The results suggested that the flexible spacers play a key role in the observed memory properties of PVK derivatives. Wang et al reported that the polyimide (**AZTA-PIa**) [20] and poly(arylene ether) (**AZTA-PEa**) [12] containing triazole structures in the main chain and triphenylamine groups in the side chain as shown below exhibited, respectively, a write-once-and-read-many-times (WORM) switching behaviors and a flash memory switching behaviors. It will be interesting and important for polymer memory materials to realize poly(ether imide)s (**AZTA-PEIa**) containing triazole structures in the main chain and triphenylamine groups in the side chain with both imide and ether structures. Functional groups are important to chemical reactions and shows different physical and chemical properties. However, to the best of our knowledge, there is no literatures discussing the memory behaviors of polymers with similar polymer backbone but with different functional linkages.

In this work, a series of functional poly(ether imide)s, **AZTA-PEI**s, containing both triphenylamine electron donor and 1,2,4-triazole acceptor groups and both ether and imide function structures were synthesized and characterized as well as the switching effects being discussed. The electronic memory behaviors of organo-soluble poly(ether imide), **AZTA-PEIa**, containing both phthalimide and ether functional groups were compared with polyimide (**AZTA-PIa**) containing imide structure, and poly(arylene ether) (**AZTA-PEa**) containing ether structure (as shown in Scheme 1). The previously reported polymer (**OXTA-PIa**) [19] showing the similar switching behavior will also compared. The imide and ether functional groups in the poly(ether imide)s playing different roles on the memory behaviors will be discussed.

2. Experimental section

2.1. Instrumentation

FT-IR spectra of the synthesized monomers and polymers were recorded on a Perkin–Elmer GX FTIR spectrophotometer. NMR spectra were measured on a Bruker DRX-500 NMR spectrometer. Elemental analyses were carried on a Perkin–Elmer 2400 elemental analyzer. The inherent viscosities of polyimides were measured with an Ubbelohde viscometer. Thermogravimetric analysis (TGA) was conducted on a Perkin–Elmer Pyris 6 TGA thermogravimetric analyzer at a heating rate of $10\,^\circ C\,min^{-1}$ and under a nitrogen or air flow rate of $20\,cm^3\,min^{-1}$. Differential scanning calorimetric (DSC) analysis was performed on a Perkin–Elmer Pyris DSC 6 calorimeter at a heating rate of $10\,^\circ C\,min^{-1}$ and under a nitrogen flow rate of $20\,cm^3\,min^{-1}$. Weight-average (M_w) and number-average (M_n) molecular weights were determined by gel permeation chromatography (GPC) on a Water GPC system equipped with four Waters Ultrastyragel columns (300×7.5 mm, guarded and packed with 10^5, 10^4, 10^3 and 500 Å gels in series). N,N-dimethylformamide (DMF, $1\,mL\,min^{-1}$) was used as the eluent which was monitored with a UV detector (JMST Systems, VUV-24, USA) at 254 nm. Polystyrene was used as the standard. UV–visible absorption and fluorescence spectra were measured on a Shimadzu UV-NIR 1601 spectrophotometer and Shimadzu RF 5301PC fluorescence spectrophotometer, respectively. Cyclic voltammetry (CV) was performed on a CHI model 619A Electrochemistry Workstation with ITO as the working electrode and a platinum wire as the auxiliary electrode at a scan rate of $50\,mV\,s^{-1}$ against a Ag/Ag^+ reference electrode in a 0.1 M acetonitrile (CH_3CN) solution of tetrabutylammo-nium perchlorate (TBAP). The thickness of the polymer film cast on the indium–tin oxide (ITO) coated glass substrate was determined from the edge profile of the film, using the tapping mode, on a Veeco multimode atomic force microscope equipped with a Nanosensors PPP-NCHR silicon tip.

2.2. Materials for synthesis

Diphenylamine, 4-aminophenol, 4-fluorobenzoyl chloride, 4-fluoronitrobenzene, acetic anhydride, and pyridine were purchased from Acros Chemical Co. and were used as received. Phosphorus pentachloride, hydrazine monohydrate, and 10% palladium on activated carbon (Pd/C) were purchased from Riedel-de Haën Chemical Co., Alfa Aesar Chemical Co., and Merck Chemical Co., respectively, and were used as received. TBAP was obtained from Acros and recrystallized twice from ethyl acetate and then dried in vacuum before use. The aromatic tetracarboxylic dianhydrides, 4,4′-hexafluoroisopropylidene- diphthalic anhydride (6FDA, **7a**; from CHRISKEV), 4,4′-sulfonyldiphthalic anhydride (SDPA, **7b**; from TCI), 4,4′-oxydiphthalic anhydride (ODPA, **7c**; from TCI), 3,3′,4,4′-benzophenone tetra-carboxylic dianhydride (BTDA, **7d**; from CHRISKEV), pyromellitic dianhydride (PMDA, **7e**; from CHRISKEV), 3,3′,4,4′-biphenyltetra- carboxylic dianhydride (BPDA, **7f**; from TCI) and were sublimated before use. N-methyl-2-pyrrolidone (NMP), N,N-dimethylacetamide (DMAc), dimethyl sulfoxide (DMSO), and toluene were purchased from Tedia Chemical Co. Tetrahydrofuran (THF) and DMF were purchased from Echo Chemical Co. 1,3-Dimethyl-3,4,5,6-tetrahydro-2(1H)-pyrimidinone (DMPU) was purchased from Aldrich Chemical Co.

2.3. Synthesis of the monomers and polymers

The synthesis routes for the monomers and polymers are illustrated in Schemes 2 and 3, respectively. The intermediate compounds **1–6** were prepared according to previously reported literature [12].

2.3.1. Synthesis of the diamine (AZTAE)

A two-necked 50-mL glass reactor with Dean-Stark trap was charged with 4-aminophenol (1.02 g, 9 mmol),