Flexible Multi-Colored Electrochromic and Volatile Polymer Memory Devices Derived from Starburst Triarylamine-Based Electroactive Polyimide

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Flexible multi-colored electrochromic and volatile memory devices are fabricated from a solution-processable electroactive aromatic polyimide with starburst triarylamine unit. The polyimide prepared by the chemical imidization was highly soluble in many organic solvents and showed useful levels of thermal stability associated with high glass-transition temperatures. The polyimide with strong electron-donating capability possesses static random access memory behavior and longer retention time than other 6FDA-based polyimides. The differences of the highest-occupied and lowest unoccupied molecular orbital levels among these polyimides with different electron-donating moieties are investigated and the effect on the memory behavior is demonstrated. The polymer film shows reversible electrochemical oxidation and electrochromism with high contrast ratio both in the visible range and near-infrared region, which also exhibits high coloration efficiency, low switching time, and the outstanding stability for long-term electrochromic operation. The highly stable electrochromism and interesting volatile memory performance are promising properties for the practical flexible electronics applications in the future.

1. Introduction

Nowadays, the application of polymeric material in optoelectronic devices has attracted tremendous attention, for example in light-emitting diodes,[1] solar cells,[2] electrochromic (EC) devices,[3] and memory devices.[4] Donor–acceptor containing polymers include both electron donor and acceptor moieties within a repeating unit, which can be switched between two conductive states via electrical field are widely researched for resistive switching memory applications recently.[4] By virtue of their flexible device structure, low cost, long range processability, three-dimensional stacking capability for high density data storage, and the possibility of modulating,[5] electrically bistable resistive switching devices based on polymeric materials have significant advantages over inorganic silicon- and metal-oxide-based memory materials.[6]

Among the different polymeric systems that have been researched, the charge transfer (CT) effect is one of the most interesting mechanisms for inducing resistor-type polymer memory (RRAM) behavior by introducing the electron donor and the electron acceptor moieties into the repeat unit of the polymer. Under an applied electric field, charge transfer will occur resulting in a transfer of electronic charge from the donor to the acceptor moiety, and the resulting structure can be defined as CT complex (CTC).[7] The stability of the CTC is regarded as one of the crucial factors for its memory behavior. Therefore, we have demonstrated the importance of structural effects tuned by incorporating different dianhydrides (electron accepter) into triphenylamine (TPA)-based polyimide backbone on the relaxation time of the polymeric memory.[8] These polyimides with different electron-withdrawing intensity revealed intriguing properties from volatile dynamic random access memory (DRAM) for **6FPI**, static random access memory (SRAM) for **PMPI** to non-volatile write-once-read-many-times (WORM) for both **DSPI** and **NPPI**, respectively. Moreover, studies based on polyimides derived from diamines having different electron-donating capability with the same electron-withdrawing dianhydride were also reported by Kang and Ree; the devices fabricated by TPA-based polyimide **TPA-6FPI**[4a] and phenylamine-substituted **2TPA-6FPI**[4b] exhibited DRAM and WORM behavior, respectively. However, the systematic research about the effect of an electron-donor moiety within a donor–accepter polyimide backbone system on the memory properties—especially for polymer memory exhibiting SRAM behavior requiring more stable CTCs resulting from the stronger electron donor—has not yet been reported.

High-performance polymers (e.g., polyimide and polyamide[4f]) containing electron donating triarylamines moiety are favorable functional materials not only for memory devices due to their excellent thermal dimensional stability, chemical resistance, mechanical strength, and high ON/OFF current ratio,[9] but also for EC applications.[10] Since 2005, our group has reported several TPA-containing anodic EC polymers

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with interesting color transitions,[10] which showed excellent EC reversibility in the visible region and NIR range. However, most of the EC polymers developed so far only revealed less than two stage EC behavior as EC devices (ECD) or were utilized for preliminary solution spectroelectrochemical investigation due to the difficulty and complexity in preparing triarylamine-containing structures with more electroactive sites. Therefore, our strategy in this work is to synthesize the starburst triarylamine-based polyimide for both polymeric volatile memory and multi-colored EC devices. By incorporating the electron-donating starburst triarylamine moiety with methoxyl-group at the *para*-position of phenyl groups, the coupling reactions of the prepared polyimide could be greatly prevented by affording stable cationic radicals with a lower oxidation potential (higher HOMO energy level).[11] The resulting electroactive polymers with high molecular weights and excellent thermal stability should be obtained readily by using conventional polycondensation. Because of the incorporation of packing-disruptive starburst triarylamine units into the polymer backbone, these novel polymers should also have excellent solubility in various polar organic solvents, thus transparent and flexible polymer thin films could be prepared easily by solution casting and spin-coating techniques. This is beneficial for their fabrication of large-area, thin-film optoelectronic devices.

In this contribution, we synthesized the aromatic polyimide containing starburst triarylamine units from the diamine monomer, *N*,*N*-bis[4-(4-methoxyphenyl-4′-aminophenylamino) phenyl]-*N*′,*N*′-di(4-methoxyphenyl)-*p*-phenylenediamine (**1**).[3b] The incorporation of electron-donating starburst triarylamine units is expected to lower the oxidation potential associated with increasing electrochemical stability and multi-stage EC characteristic. Moreover, we anticipate that the novel polyimide also could reveal more stable CTC resulting in longer retention time of memory device. Thus, the flexible multi-colored EC and polymeric memory devices were fabricated and investigated systematically in this study (**Figure 1**).

2. Results and Discussion

2.1. Synthesis and Basic Characterization of Polyimide

The new starburst polyimide **9Ph-6FDA** was prepared by the reaction of diamine **1** with commercially available 4,4′-(hexafluoroisopropylidene)diphthalic anhydride **(6FDA)** in *N*-methyl-2-pyrrolidinone (NMP) at room temperature to form the precursor poly(amic acid), followed by chemical imidization (**Scheme 1**). In the first step, the reaction mixture became very viscous as poly(amic acid) was formed, indicating the formation of high molecular weight polymer. The poly(amic acid) precursor could be chemically dehydrated to the polyimide by treatment with acetic anhydride and pyridine. The polymerization reaction proceeded homogenously and gave high molecular weight, which could afford transparent and tough films via solution casting. Polyimide **9Ph-6FDA** had an inherent viscosity of 43.0 L/mg with weight-average molecular weight (M_w) and polydispersity (PDI) of 161 800 Da and 1.94, respectively, relative to polystyrene standards (Supporting Information Table S1). The structure of polyimide **9Ph-6FDA** was confirmed by NMR and IR spectroscopy. The ^{1}H NMR spectrum was illustrated in Supporting Information Figure S1 and agreed well with the proposed molecular structure. As shown in Supporting Information

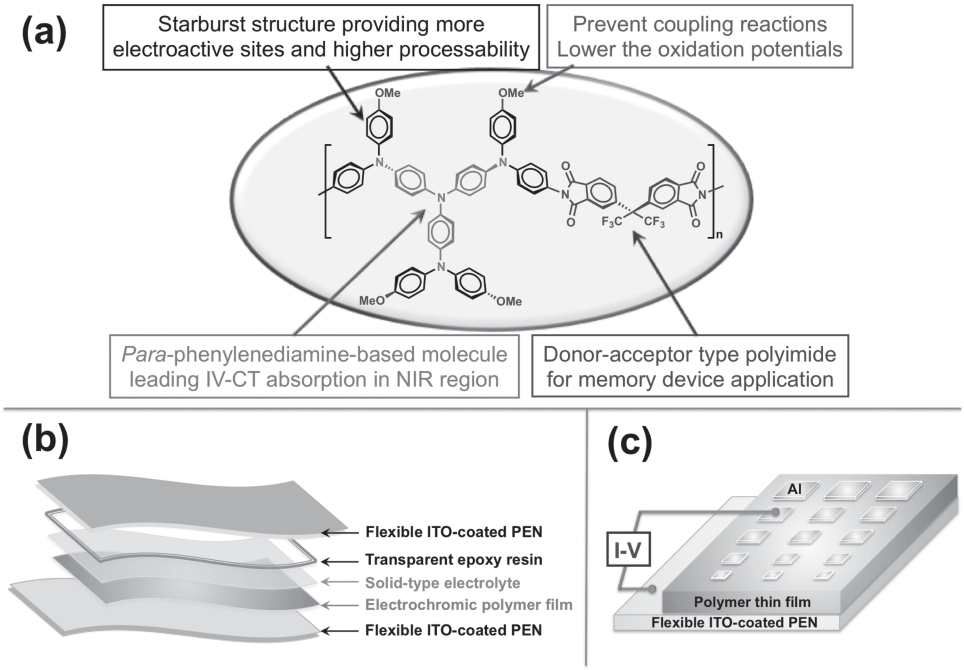

Figure 1. a) Design strategy of starburst triarylamine-based polyimide **9Ph-6FDA**, b) schematic diagram of flexible EC device based on single-layer EC polyimide, and c) configuration of the flexible memory device consisting of the polyimide thin film sandwiched between an ITO bottom electrode and an Al top electrode.

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