

## Roles of Functional Groups and Nanostructures in Advanced Polyimide Materials for Microelectronics and Displays

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### Introduction

Aromatic polyimides (PIs) are known to possess excellent thermal stability, dimensional stability, and mechanical properties. Due to these advantageous properties, PIs have found diverse applications in the microelectronics, flat panel display, aerospace, and chemical and environmental industries as flexible circuitry carriers, stress buffers, interdielectric layers, passivation layers, liquid crystal alignment layers, varnishing resins, fibers, matrix materials, and gas and chemical separation membranes. In recent years we have concentrated on developing two different categories of advanced PI materials that can meet requirements for programmable electrical memory devices and liquid crystal (LC) flat panel displays respectively. This presentation covers these research works in aspects of chemical structure including functional groups, morphological structure, properties and their relations; in particular, mechanisms to drive electrical memory behaviors, as well as mechanisms to align LC molecules are discussed in molecular level.

### Results and Discussion

A family of advanced PIs were synthesized, including electron donors, electron acceptors, and electron donor-acceptor pairs, for electrical memory devices. All the PIs were found to be amorphous but to have a certain level of tendency to preferentially orient in the film plane; furthermore their optical and electrochemical properties were characterized in detail. Their memory characteristics were evaluated mostly in a simple metal/PI/metal sandwich structure. The PIs were found to reveal a variety of electrical memory behaviors, depending on the chemical composition including functional groups, film thickness, film formation process condition, symmetric or asymmetric metal electrode pairs, temperature, and so on: unipolar and/or bipolar switchable (so-called flash) and write-once read-many times memories and dynamic random access memory, which can be operable with low threshold voltages, high ON/OFF ratios, long retention times and high reliability even in air ambient as well as up to around 200 °C.

The switching mechanisms of polymer memory devices have found to be very complicated because several properties of the material and the device combine to produce the memory behavior; the significant factors might include the molecular orbital levels, band-gap, the electron-donor group and its population and donor ability, the electron-accepting group and its population and accepting ability, the morphological structure and orientation and their changes in an applied electric field, the charge-trap ability and capacity, the stabilization of trapped charges, the trapped-charge-induced space charge field and its effects, mobile charges and their population, charge transport, polymer layer thickness, the electrode's work function, interfacial contact, electric field strength (voltage and current), and voltage sweep direction. Several switching mechanisms have been reported so far: ohmic conduction, Schottky conduction, thermionic conduction, space charge-limited conduction (SCLC), tunneling conduction, ionic conduction, polymer fuse conduction, hopping conduction, impurity conduction, local filamentary conduction, charge-transfer conduction, and conformation change conduction. The majority of the mechanisms were proposed to explain the correlations between current data and applied voltages: ohmic conduction, Schottky conduction, thermionic conduction, SCLC, tunneling conduction, ionic conduction, polymer fuse conduction, hopping conduction, impurity conduction, and so on. In general, the current levels of the ON-states of polymer memory devices are relatively high, and the variation with voltage is simple. The ohmic conduction mechanism has appeared appropriate to the current-voltage behaviors of ON-states. In contrast, other conduction mechanisms have been proposed to explain the current-voltage data for OFF-states. Current levels in OFF-states are lower than those of ON-states and, furthermore, exhibit no simple relationship with voltage. In fact, for polymers in OFF-states under an electric field, various electrical phenomena can arise, including charge injection from electrodes, charge traps, and charge flows.

Local filamentary conduction, charge-transfer, and conformation change have been proposed as explanations of electrical switching phenomena at the molecular level. In particular, local filamentary conduction mechanism has widely been adopted, which is standing on the charge-trapped sites in the polymer layer of memory device. Experimental evidence for local filament formation has been found for several polymer memory systems. When an electric field is applied to the polymer layer via electrodes, charges are trapped by the polar chemical moieties in the polymer. Such charge-trapping continues until the sites are filled completely (that is, until the applied electric field reaches the threshold voltage); the majority of these trapped charges are immobile, although some can be mobile, resulting in the low levels of current flow that are commonly observed in the OFF-state under an electric field. Above the threshold voltage, charges are excessively injected into the polymer layer and then the excessively trapped charges are able to move through the charge-trapped sites, leading to

current flows in the ON-state. Here, the charge-trapped sites in the polymer layer provide conduction paths, namely conductive filaments. In fact, the charge-trapping sites in the polymer medium cannot be in physical contact. However, charges are known to be capable of hopping a certain distance, less than approx. 1 nm. Therefore, when the charge-trapped sites are positioned with interdistances of less than 1 nm, they can act as conductive filaments, i.e., mobile charges can move between the charge-trapped sites by hopping. Overall, the memory type and performance of a polymer is primarily dependent upon its trapping sites' characteristics, including the type and number of electron-donor groups, the type and number of electron-accepting groups, the conjugated or non-conjugated links between electron-donor and electron-accepting groups, charge-trapping power and capacity, the trapped charge-induced electric field and its power and volume, and the stabilization of trapped charges. In addition, polymer layer morphology and conformation and the orientations, thickness, and molecular orbitals (highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO), band gap) of the polymer, as well as the applied electric field strength (voltage and current, often current compliance controlled) and the electrode's work function are factors that need to be considered to understand the memory type and performance of systems with local filament formation.

Another family of advanced PIs were synthesized, including various side groups and photoreactive moieties, for alignment layers in LC display devices; some parts of the PI synthesis effort have been made in collaborations with Prof. Jin Chul Jung at POSTECH and Prof. Soon-Ki Kwon at Gyeongsang National University, Korea. In the synthesis, the PI backbone was designed to be fully flexible, semiflexible, semirigid or fully rigid; furthermore the backbone was designed to include photoreactive units. On the other hand, the side group was considered to be fully flexible or semiflexible with varying its length and also to include photoreactive moieties. All the PIs were easily processable as a preimidized form or a precursor form. In rubbing process, all the PI backbones at the film surface were found to orient along the rubbing direction, whereas the side groups oriented in various manners depending on their length and flexibility (or rigidity). The rubbing-induced surface topography was varied with the PI chemical structure and properties as well as the rubbing cloth and condition. Overall, LCs were understood to interact with all possible characteristic factors of the rubbed PI film surface: mostly grooves and their orientation, and polymer backbones and side groups. In case of the PIs, the polymers generally anchor LCs on the surface via favorably interaction between the polymer itself and LC, leading to LC-alignment based on their interactions in molecular level rather than the surface topography consisting of grooves. Such favorable molecular interactions were further clearly confirmed for photoreactive PI systems.

The above two families of advanced PIs will further discussed in detail.

### Acknowledgments

This work was also supported by the National Research Foundation (NRF) of Korea (Doyak Program 2011-0028678 and Center for Electro-Photo Behaviors in Advanced Molecular Systems (2010-0001784)), and by the Ministry of Education, Science & Technology (MEST), Korea (BK21 Program and World Class University Program (R31-2008-000-10059-0)).

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