

Polybiphenylmethylenes: New Polymers for Bistable Organic Switches

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Introduction

Advances in microelectronic materials and processing techniques have pushed device sizes much smaller than micrometer dimensions. Hence, the new realm of electronic devices can be more accurately described as nanoelectronics. Phenomenon in thin film organic materials is now being used to create operational devices with active elements approaching single molecule dimensions. We have recently disclosed thin layer organic device architectures that can be used to fabricate high density storage elements – so called organic electronically bistable devices.¹ There is currently a search for polymeric materials with fine-tuned properties to enhance operation of these devices. Additionally, we also investigate conjugated polymers where applied as semiconductors² or for electroluminescent devices.³

With various transition metal catalyzed step-growth polymerization techniques in hand many, usually semiconducting, phenyl group containing polymers like PPPs, Polyfluorenes (Suzuki,⁴ Yamamoto⁵) and PPEs (Sonogashira) have been synthesized in the past decade. Monomers with aromatic bromides were utilized in most cases, less often aryl iodides, chlorides and sulfonates. Polymers with $M_n = 10,000$ g/mol are mainly yielded, which is sufficient for most applications.

We desired to explore a new class of polymeric materials containing a high content of aromatic units, specifically with short conjugated segments bridged by non-conjugated methylene units. Herein we report on the synthesis and characterization of poly(biphenylmethylene)s and their corresponding monomers. We also report the preliminary results of their electronic device characterization.

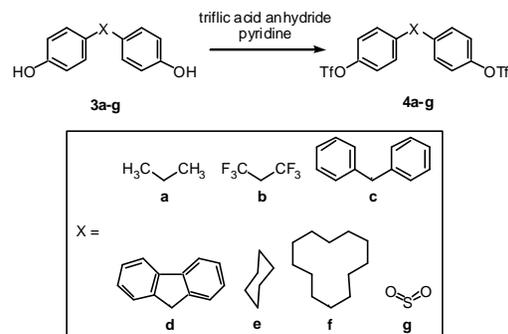
Experimental

Materials. Bisphenol A (**1a**), hexafluorobisphenol A (4,4'-hexafluoroisopropylidene)bisphenol, **1b**), bisphenol TP (4,4'-(diphenylmethylidene)bisphenol, **1c**), 4,4'-(9H-fluoren-9-ylidene)bisphenol (**1d**), bisphenol Z (4,4'-cyclohexylidenebisphenol, **1e**), trifluoromethane sulfonic anhydride (triflic anhydride), 4-bromostyrene (**4**), 4,4'-bipyridyl, and 1,5-cyclooctadiene were purchased from Aldrich or TCI and used without further purification. The Yamamoto coupling reagent bis(1,5-cyclooctadiene)nickel(0) was purchased from Strem and handled under inert atmosphere. Pyridine was used in spectroscopic grade. All nickel-mediated cross-coupling reactions were carried out under oxygen-free conditions. 4,4'-Cyclododecylidenebisphenol⁶ (**1f**) was synthesized in a way similar to the referenced protocol. 2,2-Bis(4-trifluoromethanesulfonyloxyphenyl)propane (**2a**),^{7,8} 2,2-bis(4-trifluoromethanesulfonyloxyphenyl)hexafluoropropane (**2b**),⁹ and the new monomers bis(4-trifluoromethanesulfonyloxyphenyl)diphenylmethane (**2c**), 9,9-bis(4-trifluoromethanesulfonyloxyphenyl)fluorene (**2d**), 1,1-bis(4-trifluoromethanesulfonyloxyphenyl)cyclohexane (**2e**), 1,1-bis(4-trifluoro-methanesulfonyloxyphenyl)cyclododecane (**2f**) and bis-4-trifluoromethanesulfonyloxyphenyl-sulfone (**4g**) were prepared according to a procedure described in Ref. (6) and gave satisfactory NMR, GC-MS and elemental analysis data. Published protocols were utilized for Ni(0)-mediated polymerizations: conventional heating,¹⁰ microwave assisted.¹¹

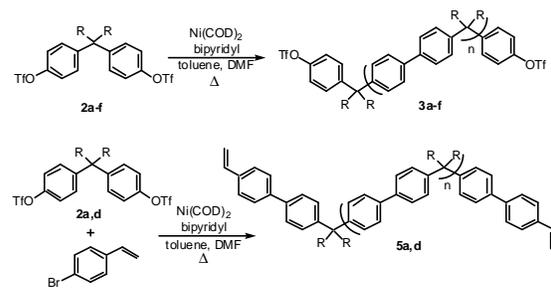
Microwave Reactor. SmithCreator, Personal Chemistry, Inc. The machine consists of a continuous focused microwave power delivery system. Reaction times and temperatures are operator selectable. Sample temperature is constantly monitored by IR, the pressure by a transducer on the top of the vial's septum, and the microwave power is automatically adjusted to maintain programmed temperature profiles.

Results and Discussion

The synthetic scheme involves the Ni-mediated Yamamoto type polycondensation (reductive aryl-aryl-coupling) of the bistriflates of bisphenol A type monomers (Schemes 1, 2). To the best of our knowledge such polymers have not yet been reported though proposed in a patent.⁷ Two kinds of poly(biphenylmethylene)s have been synthesized: homopolymers carrying triflate endgroups and styrene end-capped polymers. The endcapping procedure not only allows for some molecular weight control but also introduces a thermally crosslinkable functionality into the polymer (oligomer, respectively).^{12, 13}



Scheme 1. Monomer synthesis.



Scheme 2. Polymer synthesis.

The bistriflate monomers **2a-g** were obtained in yields >95 % by reaction of their bisphenols **1a-g** with trifluoromethane sulfonic anhydride in pyridine (Scheme 1). Column chromatography on silica gel and recrystallization ensured purities of virtually 100 % (GC-MS). Ni(0)-mediated polymerizations were carried out via two different routes. (a) Conventional heating in a Schlenk flask to 85 °C for 16 to 24 h and (b) in a microwave reactor for 10 min at temperatures ranging from 150 to 250 °C. Poly(biphenylmethylene)s **3a-f** were synthesized by both methods, the styrene endcapped derivatives **5a-f** were advantageously prepared by copolymerization of the bistriflates and 4-bromostyrene (**4**) applying method (a) (Scheme 2). Typical yields for both methods were between 50 and 85 % (THF soluble fractions) giving materials with M_n of 3000 to 8000 g/mol and DPs of 10 to 25 (not optimized reaction conditions).

Polymers **3a-f** show good thermal stability. Less than 5 % weight loss values above 350 °C were observed by thermal gravimetric analysis (TGA, 10 °C/min). The absorption and photoluminescence behaviour for polymers **3a-f** and **5a,d** were measured on thin films on quartz substrates. The absorption spectra all show two broad, featureless bands with λ_{max} ranging from 210 to 225 nm and 270 to 290 nm, respectively. In most samples, the emission spectra exhibit also two broad, featureless bands with varying intensities and λ_{max} ranging from 315 to 325 nm and at about 405 nm, respectively.

The optical and electrical properties of thin films of the polymers were examined. The absorption and photoluminescence spectrum of

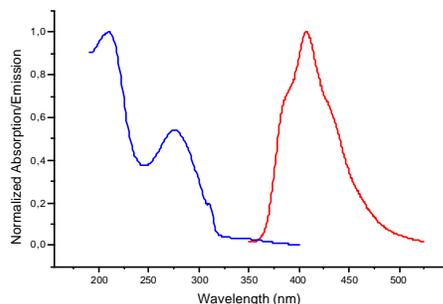


Figure 1. A typical solid state absorption and photoluminescence spectrum (polymer 5d).

polymer 5d is shown in Figure 1. All absorption spectra of polymers 3 and 5 (thin films on quartz wafer) show two broad, featureless bands with λ_{max} ranging from 210 to 225 nm and 270 to 290 nm, respectively. In most samples, the emission spectra exhibit two broad, featureless bands with varying intensities and λ_{max} ranging from 315 to 325 nm and at about 405 nm.

The electrical properties of these wide band gap materials were studied by preparing and characterizing thin film test devices. These thin layer devices were prepared by spin coating thin films (ca. 50-500nm) of the polymers from solution onto ITO substrates. Aluminium was then evaporated on top of the polymer layer(s). A schematic representation of the devices with corresponding energy band diagram is shown in Figure 2. Polymers 3 and 5 have band gaps of $E_g = 4.3$ to 4.8 eV, as estimated from their absorption max. The actual ionization potential energy value has not been determined experimentally. By comparison, polyfluorenes, which are well known and used for the fabrication of OLED devices have an $I_p \sim 5.5$ eV, $E_g \sim 3.0$ eV.

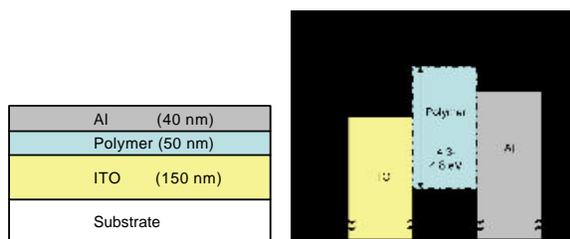


Figure 2. Depiction of the device structure (left) and its energy band diagram (right).

The IV curve from a device prepared from 5d is shown in Figure 3. Polymers 5b and 5d were shown to exhibit low current flow when operated in a organic diode configuration. This could indicate either high resistance of the bulk material or low charge injection at the metal polymer interface.

When single layer or multiplayer devices were prepared containing gold nanoparticles, bistable electrical behavior was observed.¹ The devices operation is shown in Figure 4. Initially the device is in a high resistance state, curve 1, until a critical switching voltage is reached ($V_{Switch} = 2V$) at which point the device switches to a stable low resistance state (curve 2). The device will remain in this low resistance state until a resetting voltage is applied ($V_{Reset} = 4.5V$).

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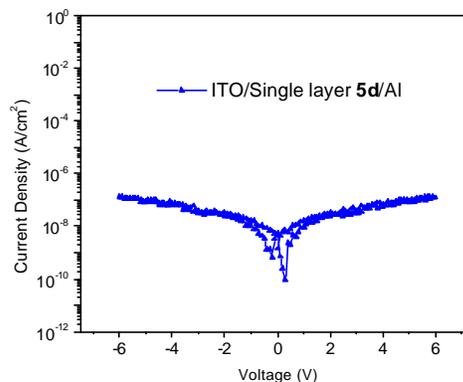


Figure 3. IV curve for single layer device made from 5d.

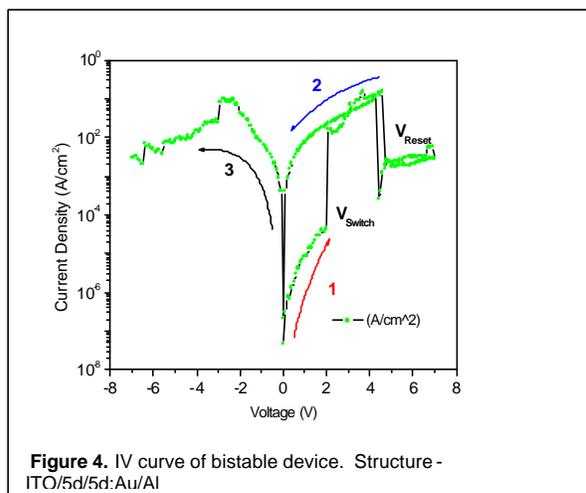


Figure 4. IV curve of bistable device. Structure - ITO/5d/5d: Au/Al

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