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A New Humidity-Sensitive Material Based on PPBT Prepared with Palladium Complex Catalyst

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Abstract: Soluble Poly(propargyl benzoate) (PPBT) with π-conjugated structure was synthesized using a novel bis(triphenylphosphine)-bisacetylide palladium complex catalyst $[Pd(PPh_3)_2(C{\equiv}CCH_2OOCPh)_2]$ (PPB). An interdigital gold electrode was covered by screen printing films of doped PPBT (DPPBT) to prepare a resistance-type humidity sensor, which exhibits electrical response towards relative humidity (RH%) variations in the range 11%-96%. PPBT shows promise as a new humidity-sensitive material.

Keywords: Humidity-sensitive materials, poly(propargyl benzoate), bis(triphenylphosphine)-bis-acetylide palladium complex, resistance-type humidity sensor.

Introduction

In recent years, there has been an increasing interest in humidity sensors in various fields such as air-conditioning systems, medical and industrial equipment, *etc*. The research on humidity sensors, which focused on looking for suitable polymeric humidity-sensitive materials, has attracted more and more attention with some encouraging results[1].

Poly(propargyl benzoate) is a hydrophilic polymer with π-conjugated structure. In the past 30 years, the synthesis of poly(propargyl alcohol) (POHP) and its derivatives, as one kind of substituted polyacetylenes, has been intensively investigated[2-3]. But, such efforts have met with only limited success. For example, polymerization of functional acetylene monomers containing hydroxyl (-OH) group usually gave either cyclicoligomers[4] or insoluble products[5], normally in low yields. Moreover, there is few report referred to the polymerization of propargyl benzoate. Recently, we succeeded in developing a new palladium catalyst, which meaningfully improved the synthesis conditions and the solubility of POHP, for the homogeneous polymerization of propargyl alcohol (OHP)[6]. The polymer obtained exhibits good humi-sensing characteristics for the first time after being doped with sulfuric acid[7].

In the present paper some results concerning the synthesis and characterization of PPBT prepared with a new palladium acetylide complex and preliminary investigations

regarding its use as a humi-sensing material in a resistance-type humidity sensor are reported.

Experimental

Preparation of $Pd(PPh_3)_2(C{\equiv}CCH_2OOCPh)_2$ (PPB)

0.218 g (0.31 mmol) of $Pd(PPh_3)_2Cl_2$[6], 0.005 g (0.026 mmol) of CuI, and 10 ml of $HNEt_2$ were introduced into a reaction vessel. Meanwhile the mixture was stirred at room temperature, 0.36 ml (1.22 mmol) of propargyl benzoate[8] was added dropwise into the vessel. After 30 minutes, the color of precipitate changed from yellow to white. The precipitate was filtered and washed with $HNEt_2$ and EtOH, and dried in vacuum at room temperature for 8 h. The yield is 87% (decomposition point, 144-145°C). IR (cm^{-1}): 2128 (C≡C), 1705 (C=O), 1270 (C-O), 720, 690. For $PdO_4P_2C_{56}H_{44}$, calculated (%): C, 70.85%, H, 4.67%; Found: C 70.85%, H, 4.74%.

Preparation of PPBT

All procedures for polymerization are carried out under purified nitrogen atmosphere. A topical polymerization procedure is as follows: into a 30 ml well-dried ampoule, 0.03979 g (0.042 mmol) of PPB , 1.0 ml of chlorobenzene were added in turn, shaken (≤ 50°C) to obtain a homogenous solution, and then, 0.5 ml (3.34 mmol) of propargyl benzoate (PBT) was injected. The mixture was aged at 80°C for 10 h, then ethyl ether was added to get a precipitate, which was filtered, washed with ethyl ether, and dried under vacuum at room temperature for 8 h. The polymer is brown with a yield of 72%. IR (cm^{-1}): 1655 (C=C), 1720 (C=O), 1270 (C-O), 955, 940,690, 710. UV ($\lambda_{max,}$nm): 370.

Doping of PPBT

The doping of PPBT was carried out by dipping 0.72 g of PPBT powder into 16 ml THF, in which 0.28 g (1.73 mmol) of $FeCl_3$ was previously dissolved. The resulting solution was aged at 40°C for 24 h, then the doped PPBT (DPPBT) was precipitated as a black powder by addition of ethyl ether. The precipitate was filtered and dried under vacuum for 8 h.

Preparation of humidity sensor and testing of humidity response

The humidity sensor was prepared by screen-printing DPPBT pastes on an interdigital gold electrode with spaces of 80 μm between tracks. The paste was prepared by mixing up milled DPPBT with organic vehicle (conductive glue and its diluent). The electrical characteristics of DPPBT as a function of relative humidity was tested with a digital multimeter (applied a.c. voltage=3V, f=1KHz, 25°C). Different relative humidity values (RH%) were obtained by various saturated salt solutions.

Results and Discussion

The $Pd(PPh_3)_2(C{\equiv}CCH_2OOCPh)_2$ (PPB) is a new catalyst for the polymerization of propargyl benzoate (PBT). It is found that the polymerization system shows high activity in chlorinated hydrocarbon, such as chloroform, chlorobenzene, and 1,2-dichloroethane. Among them, chlorobenzene is the favorable one for the homogeneous polymerization of PBT. The polymer yield reaches 72% in chlorobenzene at 80°C for 10 h polymerization while the monomer and catalyst concentration is 2.23 mol/L and 0.028 mol/L, respectively. The polymer obtained is a brown powder with π-conjugated structure, having a molecular weight (Mw) of 3370, good solubility and air stability. DPPBT is a black powder with worse solubility compared with PPBT. IR spectrum of this material reveals a lowering of the C=C frequency (1610cm^{-1}), reasonably due to the interaction between the dopant and the polymer chain.

Figure 1. Humidity response of sensors based on PPBT(°) and DPPBT(•), respectively.

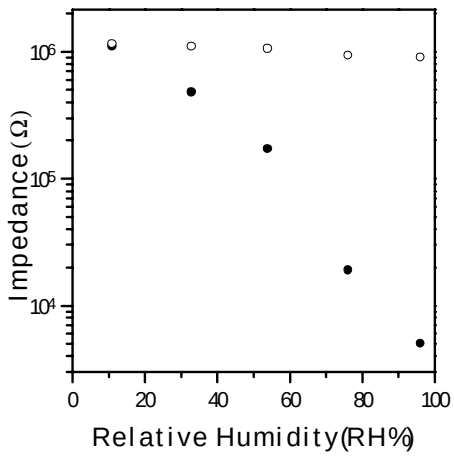

Figure 1 shows the humidity response of the sensors based on PPBT and DPPBT, respectively, at different relative humidity (RH%). It is seen that the undoped PPBT shows almost no response to relative humidity variation. However, the impedance of the sensor based on $FeCl_3$-doped PPBT changes from 5 KΩ to 1150 KΩ while the relative humidity decreases from 96% to 11%, and the sensor has a high sensitivity (12.9 KΩ/RH%). All the preliminary results indicate that PPBT is a promising new material for a resistance-type humidity sensor. Further research with focus on improving its sensitivity and repeatability is in progress.

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