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Polycarbonate films metalized with a single component molecular conductor suited to strain and stress sensing applications

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ABSTRACT

The paper reports all-organic strain and stress sensitive films that use electrical monitoring approach. The films were prepared by self-metallizing polycarbonate films with the single component molecular conductor $[Au(\alpha\text{-tpdt})_2]^0$ (tpdt = 2,3-thiophenedithiolate). It was shown that $[Au(\alpha\text{-tpdt})_2]^0$ by its nature is able to form metallic solid material with low crystallinity. Electromechanical tests demonstrated that the developed films are strain-resistive materials with advanced elastic properties: their electrical resistance varies linearly with uniaxial elongation up to relative strain being of 1.0% that is about five times larger than that for conventional metals. The gauge factor of the films is 4.4 and stress sensitivity is 30 Ω/bar. The processing characteristics of polycarbonate films, self-metalized with a metallic $[Au(\alpha\text{-tpdt})_2]^0$-based layer, make them potentially useful for engineering flexible, lightweight, strain and pressure sensors. Due to electromechanical characteristics these films are suited to strain sensing applications requiring miniature strain control in a wide deformation range.

1. Introduction

The development of metalized plastics, whose electrical transport properties strongly respond to delicate strain, brings great opportunities in the field of strain, pressure or bending sensors for their applications as human–machine interfaces, intelligent textiles, robotic interfaces and body sensing devices [1–3]. In this context the polycarbonate films covered with a thin layer of an organic molecular conductor are attracting large attention due to their ability to combine properties such as electrical conductivity, high sensitivity to strain (pressure), lightweight, and flexibility [4–7]. Recently it was also shown that these films can be integrated in textiles [8]. In relation to this topic, the single component molecular conductor $[Au(\alpha\text{-tpdt})_2]^0$ (tpdt = 2,3-thiophenedithiolate) (Fig. 1), which was early reported from some of us, [9] is very attractive for metallization of polymeric films for two reasons. First its powder-like sample displays some properties of a metallic system with a very high value of room temperature electrical conductivity and, second, by its very nature, the single component conductor $[Au(\alpha\text{-tpdt})_2]^0$ is able to form a conductive covering layer in a low crystallinity state [9]. An amorphous conducting layer is an important purpose to be achieved because an amorphous state will be able to keep conductive covering layers free from problems associated with polymorphism and grain boundaries [10].

Here we demonstrate that metallization of polycarbonate films with the single component molecular conductor

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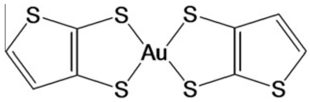

Fig. 1. Chemical structure of $[Au(\alpha\text{-tpdt})_2]^0$.

$[Au(\alpha\text{-tpdt})_2]^0$ permits engineering flexible lightweight strain (pressure) sensing organic materials that use electrical monitoring approach. We also present experimental data on the metallic nature of resistance temperature dependence of $[Au(\alpha\text{-tpdt})_2]^0$-based covering layers. Additionally, the tensile tests showing that developed films reveal advanced electromechanical and elastic properties are presented and discussed.

2. Experimental

2.1. Materials

Experimental Materials from "Aldrich", such as pellets of Poly(Bisphenol A carbonate) (Polycarbonate, PC, average M_w ca. 64,000), 1,2-chlorobenzene and dichloromethane, were used as received. Both solvents were of an anhydrous standard (99.8%) packed under nitrogen.

Precursors of the single component molecular conductor $[Au(\alpha\text{-tpdt})_2]^0$, such as tetra alkyl ammonium salts: $[(C_2H_5)_4N]^+[Au(\alpha\text{-tpdt})_2]^-$ and $[(C_4H_9)_4N]^+[Au(\alpha\text{-tpdt})_2]^-$, were synthesized as previously described [9].

2.2. Metallization of polycarbonate films with $[Au(\alpha\text{-tpdt})_2]^0$

A set of 25–30 μm thick films have been prepared on a glass support at 130 °C. The films comprising a 97 wt.% of PC and 3 wt.% of $[(C_4H_9)_4N]^+[Au(\alpha\text{-tpdt})_2]^-$ were cast from a 1,2-dichlorobenzene solution that contains a 2 wt.% of PC and 0.1 wt.% of $[(C_4H_9)_4N]^+ [Au(\alpha\text{-tpdt})_2]^-$. The film surface was treated with vapors of a saturated solution of I_2 in CH_2Cl_2 during 6–8 min at 23 °C. Detailed data on this metallization procedure are presented in ESI (Fig. S1 and Table S1).

2.3. Composition and texture of the covering layer

(a) The elemental analysis of the covering layers was performed with a scanning electron microscope (SEM) "Quanta FEI 200 FEG-ESEM" with an EDX-EDAX instrument operating at 10 kV. The $[(C_4H_9)_4N]^+[Au(\alpha\text{-tpdt})_2]^-$ salt was used as a standard.

(b) Surface analysis on micro scale was performed using a SEM "Quanta FEI 200 FEG-ESEM". SEM images of different magnifications were acquired at 20 kV.

2.4. X-ray diffraction (XRD) patterns

To study the structures of the covering layers of $[Au(\alpha\text{-tpdt})_2]^0$, film samples with 2.3 cm^2 were attached to a glass support and their X-ray diffraction patterns were recorded on a Rigaku "Rotaflex" RU-200B diffractometer in reflection mode with monochromatic Cu*K*α radiation (λ = 1.540598 Å); The generator was activated at 50 kV and 80 mA.

2.5. Macroscopic electro-transport properties

The values of the room temperature resistance of BL films as well as their resistance temperature dependences were measured by a standard four-probe dc-method. Rectangular pieces (4×2 mm^2) were cut out from the film samples, and four annealed platinum wires with a diameter of 20 μm were attached to a conducting covering layer of BL films with a conductive graphite paste.

2.6. Microscopic transport properties

The resistance and topography were simultaneously mapped in current-sensing mode on a commercial Agilent 5100 scanning force microscope (AFM) by scanning a biased tip that was maintained in contact with the sample surface; *I–V* responses were acquired by scanning locally the dc current through the tip–sample junction while sweeping the applied bias voltage.

2.7. Mechanical and electromechanical test

Mechanical and electromechanical properties of the films were studied using a 5848 MicroTester with a 1 kg load cell (Instron). Tester was additionally equipped with two electrical contacts and the resistance change under tensile testing was monitored using an Agilent 34410 A; film strips in dimension of ca. 28×2 mm^2 and free from physical imperfections, were held between two clamps positioned at a distance of ca. 18 mm. During measurement, the strips were pulled by the top clamp with velocity being 2.0 μm/s. Measurements were run in two replicates for each film.

3. Results and discussion

3.1. Metallization of polycarbonate films with $[Au(\alpha\text{-tpdt})_2]^0$

The metallization procedure used here is closely related to a simple synthetic method developed for surfacing polycarbonate films with conducting charge-transfer salts [4,11,12]. The metallization is a single-stage procedure, which involves two consecutive processes: (1) an internal oxidation of $[Au(\alpha\text{-tpdt})_2]$-based precursor introduced in a polycarbonate film (reaction 1) and (2) self-assembly of single component molecular conductor $[Au(\alpha\text{-tpdt})_2]^0$ as a metallic topmost layer.

$$2[(C_4H_9)_4N]^+[Au(\alpha\text{-tpdt})_2]^- + I_2 = 2[Au(\alpha\text{-tpdt})_2]^0 \downarrow + 2([(C_4H_9)_4N]^+I^-) \qquad \text{(reaction 1)}$$

In line with the method (ESI, Fig. S1) we first prepared 25–30 μm thick polycarbonate films spiced up with a 3 wt.% of the $[(C_4H_9)_4N]^+[Au(\alpha\text{-tpdt})_2]^-$ salt that is a precursor for $[Au(\alpha\text{-tpdt})_2]^0$. To metalize the films with $[Au(\alpha\text{-tpdt})_2]^0$, we exposed one of their surfaces to vapors of a saturated solution of iodine in dichloromethane. The formation of conductive covering layers was tested by direct current (dc) conductivity measurements. (ESI, Table S1). The composition of the conductive layers was studied by EDX analysis. The S:Au stoichiometry of the layers varies from 6:1 to

6.4:1, close to the calculated value for [Au(α-tpdt)$_2$]: $C_8H_4AuS_6$. The EDX data also showed the presence of iodine in the surface of the covered films: the ($C_8H_4AuS_6$):I proportion varies from 1:0.7 to 1:1,2, approaching the value 1:1, as it should be if reaction 1 occurred in the swollen surface. The lack of characteristic bands corresponding to ν_{I-I}, $\nu_{[I-I\cdots I]^-}$ $\nu_{[I-I\cdots D]^-}$ and $\nu_{[I-I-I]^-}$ vibration modes [13,14] in the low frequency Raman spectra of the developed films suggests that iodine did not form I_3^- anions as well as any adducts bonded with the conductive covering layer and polycarbonate molecules. One may suggests that iodine exists entirely as I^- anions, being combined with the $[(C_4H_9)_4N]^+$ cations due to strong Coulomb interactions. It is likely that the molecules of the $[(C_4H_9)_4N]I$ salt are aggregated deep in the treated film surface.

3.2. Texture and structure of the [Au(α-tpdt)$_2$]^0-based layers

The texture and crystalline state of the [Au(α-tpdt)$_2$]^0-based layers were studied by SEM and X-ray powder diffraction, respectively. The SEM images of the conductive layers mainly reveal close packed needle- and plate-like morphologies with sizes up to hundred nanometers (Fig. 2, ESI, Figs. S2 and S3).

The XRD spectra of the [Au(α-tpdt)$_2$]^0-based layers (Fig. 3 and ESI, Figs. S4 and S5) show a wide intensive diffusing halo at 15° < 2θ < 35° that differs in its shape from that of the reference PC film (Fig. 3, insert). The lack of well-definite reflections in the film patterns suggests that the conductive covering layers are formed by the [Au(α-tpdt)$_2$]^0 conductor with low crystallinity. Therefore, [Au(α-tpdt)$_2$]^0 lived up to our expectations as a candidate for preparing conductive amorphous covering layers.

3.3. Electrical transport properties of [Au(α-tpdt)$_2$]^0-based active layer

The four probe dc measurements of resistance *versus* temperature revealed that the number of continuous metallic paths extending through the conductive covering layers, is enough to show metal-like macroscopic electrical transport properties at T > 280 K (Fig. 4, ESI, Fig. S6). This result is an additional proof that the single component conductor [Au(α-tpdt)$_2$]^0 is a metallic system, as claimed in Ref. [9]. Furthermore, [Au(α-tpdt)$_2$]^0 is able to form a metallic interconnection network uniquely in the thin layer prepared by the above method that is an advantage over polycrystalline samples of [Au(α-tpdt)$_2$]^0 which show semiconductor-like temperature-dependent electrical resistance due to interparticle resistance effects [9].

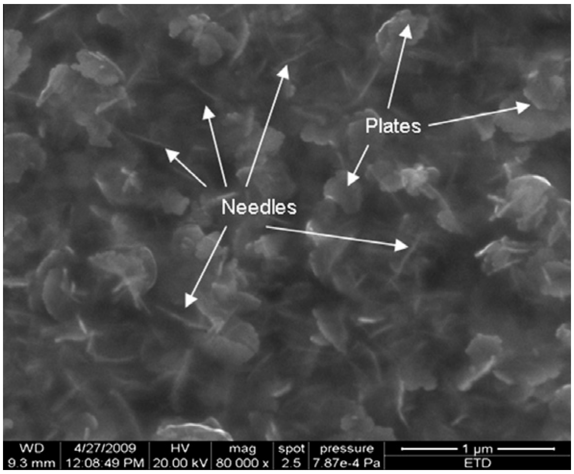

Fig. 2. SEM image monitored from the conductive [Au(α-tpdt)$_2$]^0-based covering layer.

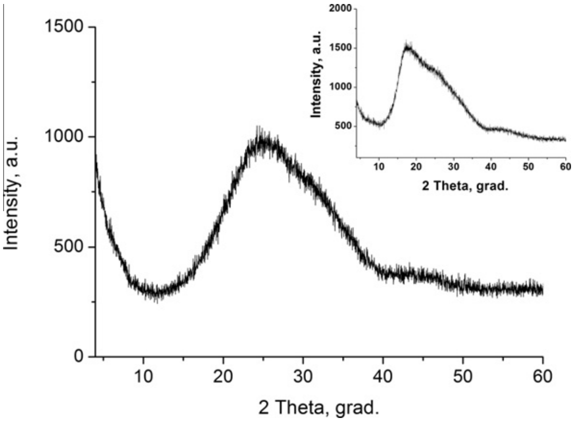

Fig. 3. The typical XRD pattern of the conductive [Au(α-tpdt)$_2$]^0-based covering layers; inset shows the XRD spectrum of a reference polycarbonate film.

The homogeneity of the electrical conduction of the [Au(α-tpdt)$_2$]^0-based layer at the microscopic scale was confirmed by the results from CS-AFM studies: in most

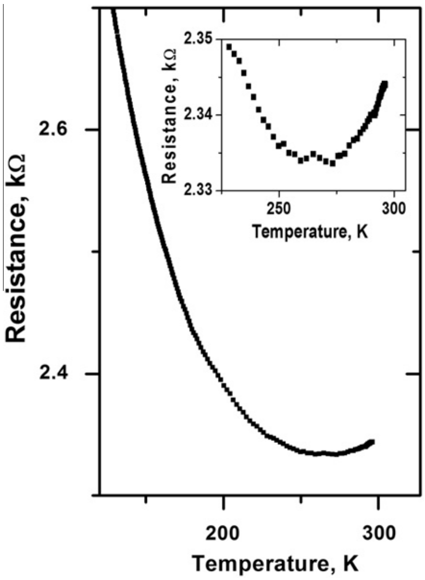

Fig. 4. Temperature dependence of the electrical resistance of the polycarbonate film self metalized with [Au(α-tpdt)$_2$]^0; insert: zoom of R(T) dependence showing metallic behavior of the [Au(α-tpdt)$_2$]^0-based layer.

cases the *I–V* responses recorded from the covering layers show an ohmic character with conductance of about 20 μs (Fig. 5).

3.4. Mechanical and electromechanical properties

We studied the responses of the films covered with $[Au(\alpha\text{-tpdt})_2]^0$ to unidirectional stress to provide an overview of their mechanical and electromechanical properties. For this purpose their tensile testing in the elastic range was coupled with direct resistance measurements. For reference, a 25 μm thick polycarbonate film was also prepared and tested (ESI, Fig. S7). The tensile tests (Fig. 6 and ESI, Fig. S7) showed that the metallization of polycarbonate films with $[Au(\alpha\text{-tpdt})_2]^0$ tends to decrease the value of Young's Moduli (E) of a polycarbonate film from 2.05 to 1.70 GPa. The metallization also reduced moderately the value of the polycarbonate elastic limit (ε_{Yield}) from 1.4% to 1.2%. In spite of the above mentioned minor differences, the mechanical characteristics of the developed films are close to those of the reference polycarbonate film (ESI, Fig. S7). Therefore, the metallization of polycarbonate with $[Au(\alpha\text{-tpdt})_2]^0$ did not adversely affect its mechanical properties.

Fig. 6 also shows that resistance changes *versus* strain deviate from linear proportionality at the relative strain (ε) of 1.0%, $\varepsilon = (L - L_0)/L_0$, were L_0 and L are the lengths of the film-based gauge without and under elongation, respectively. By analogy with the elastic limit point, this point can be termed as the resistance proportional limit of the bi layer (BL) film (R_{yield}). The sensitivity of the films to stress was calculated as 30 Ω/bar. The nonlinearity above R_{yield} can be associated with small numerous strain nanocracks formed perpendicularly to an elongation direction [15] and, therefore, R_{yield} of the developed BL films corresponds to the elastic limit point of the metallic $[Au(\alpha\text{-tpdt})_2]^0$-based covering layer. The fact that the value of R_{yield} of polycarbonate films metalized with $[Au(\alpha\text{-tpdt})_2]^0$ is closely related to that of ε_{Yield} has to impart a good robustness to flexible sensors based on the developed films. These BL films surpass the recently reported highly piezo-resistive films [6] in elasticity; the same tensile tests showed that the value of R_{yield} for the polycarbonate metalized with organic molecular metal $\beta\text{-}(ET)_2I_3$ is only 0.65% (ET = bis(ethylenedithio)tetrathiafulvalene). Therefore, polymeric films covered with a metallic layer showing low crystallinity can significantly enhance the resistance proportional limit of BL films and extend their capabilities of monitoring different deformation.

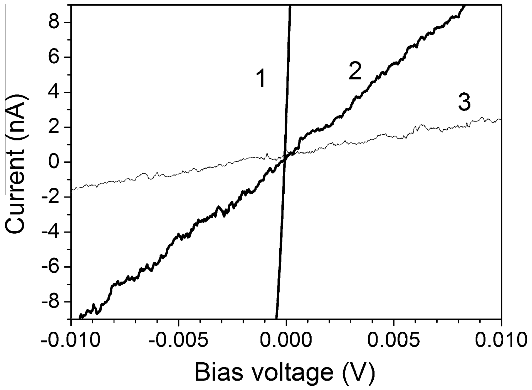

Fig. 5. The ohmic *I–V* responses measured at different locations.

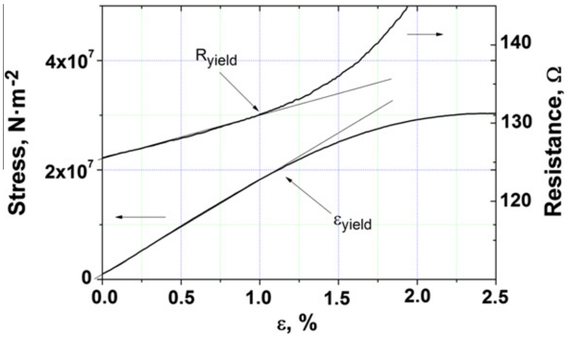

Fig. 6. Stress–strain and resistance-strain curves for the polycarbonate film metalized with $[Au(\alpha\text{-tpdt})_2]^0$.

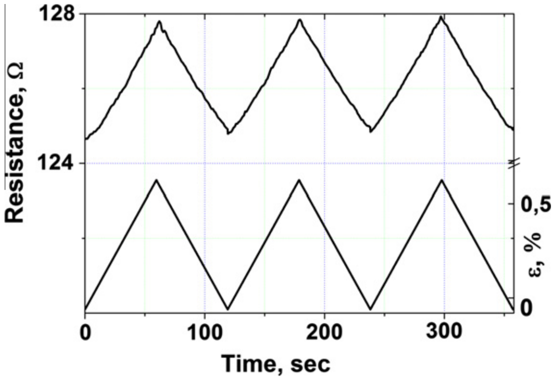

Fig. 7. Resistance response of metallic covering layer of $[Au(\alpha\text{-tpdt})_2]^0$ to cyclic elastic elongations with $\varepsilon_{max} = 0.65\%$.

As shown in Fig. 7, the electrical response of the metalized films to multi-cyclic monoaxial elongation carried out in the elastic range of deformation is very reproducible and linearly depends on relative strain. The gauge factors, calculated as the ratio between the relative resistance change and the relative strain value, were found to be 4,4. This value is less then that reported for highly piezo-resitive BL films, [6] however, it match the gauge factor of Pt that shows the most pronounced strain resistive effect among inorganic metals [16].

4. Conclusions

It has been developed a polymeric material covered with a metallic layer of the $[Au(\alpha\text{-tpdt})_2]^0$ conductor with low crystallinity that offers new opportunities to engineering flexible all-organic conducting materials with advanced electromechanical properties. Due to the low crystallinity of $[Au(\alpha\text{-tpdt})_2]^0$, the elastic deformation range of the $[Au(\alpha\text{-tpdt})_2]^0$-based layer is nearly twice as large as that for reported piezo-resistive polycrystalline layers based on two component organic molecular conductors. It was also shown that the polycarbonate films metalized with $[Au(\alpha\text{-tpdt})_2]^0$ reveal a well pronounced piezoresistive effect.

Both simple synthetic procedure and advanced electromechanical characteristics of the developed piezo-resistive BL films make them well suited to strain and stress sensing applications were flexibility and lightweight are required.

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Supporting Information is available online from the Journal or from the authors.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.orgel.2012.01.031.

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