

# One-pot photoinduced synthesis of conductive polythiophene-epoxy network films

Marco Sangermano<sup>a,\*</sup>, Federica Sordo<sup>b</sup>, Alessandro Chiolerio<sup>c</sup>, Yusuf Yagci<sup>d,e</sup>

<sup>a</sup> Politecnico di Torino, Dipartimento di Scienza dei Materiali e Ingegneria Chimica, C.so Duca degli Abruzzi, 24 I-10129 Torino, Italy

<sup>b</sup> Laboratoire de Technologie des Composites et Polymères (LTC), Ecole Polytechnique Fédérale de Lausanne (EPFL), Station 12, CH-1015 Lausanne, Switzerland

<sup>c</sup> Istituto Italiano di Tecnologia, Center for Space and Human Robotics, C.so Trento 21, 10129 Torino, Italy

<sup>d</sup> Department of Chemistry, Istanbul Technical University, Maslak 34469, Istanbul, Turkey

<sup>e</sup> Faculty of Science, Chemistry Department, King Abdulaziz University, Jeddah, Saudi Arabia

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## ABSTRACT

In this paper, we describe a novel methodology for fabricating conductive epoxy-polythiophene network films by simultaneous photoinduced step-growth and cationic ring opening polymerization processes. For this purpose, formulations containing a bifunctional epoxy monomer, namely 1,6-hexanediol diglycidyl ether (HDGE) and different amount of thiophene ranged from 0 to 50 wt% in the presence of an iodonium salt, namely (4-methylphenyl)[4-(2-methylpropyl) phenyl]-iodonium, hexafluorophosphate were irradiated under UV light. In the process, while polythiophene was formed through electron transfer reaction between photochemically formed phenyliodonium radical cations followed by proton release and coupling reactions, cationic ring opening polymerization of HDGE initiated by the liberated protons resulted in the formation of epoxy network. Conductivity of the obtained films was evaluated by surface resistivity measurements by means of a standard two-point micro-contact method before and after iodine doping. It was found that iodine doping provided a significant improvement in the surface conductivity. This work conclusively provides a new approach for bonding conducting polymers with epoxy-based network films via photoinduced electron transfer reactions in a simple, fast, and efficient approach of importance in electronic and other applications.

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## 1. Introduction

Polymer films are a promising candidate for the realization of flexible electronics, due to their easy processability, low cost and availability [1]. The main limit in their application is related to the very high surface resistivity. There are many report in literature focused on the preparation of conductive polymeric coatings.

In general, two main strategies concerning preparation of organic resistor films having a typical resistivity in the range  $10^4 \Omega \text{ cm} - 10^3 \Omega \text{ cm}$  are distinguished:

- (i) addition of conductive fillers up to percolation threshold into polymeric matrix [2–5],
- (ii) use of intrinsic conductive polymers [6].

UV-Curing technique receives broad research interest because of its wide range applicability in coating technologies with economic and ecological anticipations [7].

\* Corresponding author.

E-mail address: [marco.sangermano@polito.it](mailto:marco.sangermano@polito.it) (M. Sangermano).

This polymerization technique allows obtaining a fast transformation of a liquid monomer into a solid film with tailored physico-chemical and mechanical properties. In the case of the cationic polymerization, onium salts are used as photoinitiators to generate strong Brønsted acids capable of initiating polymerization of appropriate monomers such as oxiranes and vinyl ethers [8]. Compare to the radical mode, the cationic process presents some advantages [9,10], in particular lack of inhibition by oxygen, low shrinkage, good mechanical properties of the UV cured materials and good adhesion properties to various substrates. Moreover, the monomers employed are generally characterized by being less toxic and irritant.

One way to obtain conductive coatings by photochemical means is the dispersion of carbon nano tubes (CNT) as conductive fillers in UV curable epoxy formulations [11,12]. Highly cross-linked epoxy network characterized by high gel content and good mechanical properties were readily obtained by UV irradiation.

The surface resistivity of cured films was investigated and it was shown that the material was transformed from an electrical insulating into a dissipative one at already 0.025 wt% CNT content.

Alternative approach concerns the concomitant redox and polymerization processes by using certain metal salts such as silver

(Ag) and gold (Au) salts at their higher oxidation states and free radical photoinitiators. The approach was successfully applied [13–19] to both free radical and cationic systems based on acrylates and epoxides, respectively. In the process, while metal nanoparticles were formed by electron transfer from the photochemically generated free radical to the salts, polymerizations were initiated by free radicals or carbocations thus formed depending on the type of monomers used in the formulation. However, despite the success of the process, it was possible to reach conductive surface behavior only for large metal NPs precursor contents, which would affect strongly the processability and cost of the formulations [4,5].

Although conducting conjugated polymers, in particular those based on thiophene and derivatives, are extensively used in the fabrication of electronics and electro-optic devices arising from characteristic electronic and optical properties [20–22], their preparation by photochemical means has scarcely been investigated. Yagci and co-workers demonstrated that polythiophene can be obtained by UV irradiation using onium salts as light absorbing compounds [23]. As evidenced by laser flash photolysis and EPR studies, the step-growth polymerization involves electron transfer from photochemically generated phenyliodonium radical cations to thiophene [24]. The approach was further extended to the near UV and visible region of electromagnetic radiation by using highly conjugated thiophene derivatives in the system [25]. Detailed laser flash photolysis, fluorescence and phosphorescence spectroscopy studies [26] revealed that the reactive thiophene radical cation was produced within the exciplex formed between excited thiophene and iodonium salt as presented in Scheme 1.

In another study, *in situ* photoinduced oxidation of pyrrole to polypyrrole was successfully employed to form an acrylic UV-crosslinked network characterized by surface conductivity [27].

Herein, we introduce a method to fabricate conductive epoxy networks, the conductivity of which is controlled by the amount of thiophene and subsequent doping process. As will be shown below, step-growth polymerization of thiophene and cationic curing of a bisepoxide proceed simultaneously to yield desired conductive films.

## 2. Experimental

### 2.1. Materials

Epoxy resin, 1,6-hexanediol diglycidyl ether (Araldite DY-H/CH, HDGE) was purchased from Huntsman. (4-Methylphenyl)[4-(2-methylpropyl) phenyl]-iodonium, hexafluorophosphate (Irgacure 250), a liquid cationic photoinitiator (75% solution in propylene carbonate) was supplied from BASF, while thiophene (Th) and iodine were purchased from Sigma–Aldrich. All the chemicals were used as received.

### 2.2. Film preparation

Epoxy based formulations were prepared by mixing the epoxy resin with Th in the range between 85:15 to 50:50 wt/wt. A given amount of cationic photoinitiator was added and homogenous formulations were obtained through a mechanical mixing.

The formulations were poured in closed glass molds and UV irradiated at a light intensity of 50 mW/cm<sup>2</sup> under nitrogen atmosphere. The same preparation and irradiation procedures were followed to produce a second group of materials that were subsequently iodine doped by their exposure to iodine fumes in a closed drier for 6 h.

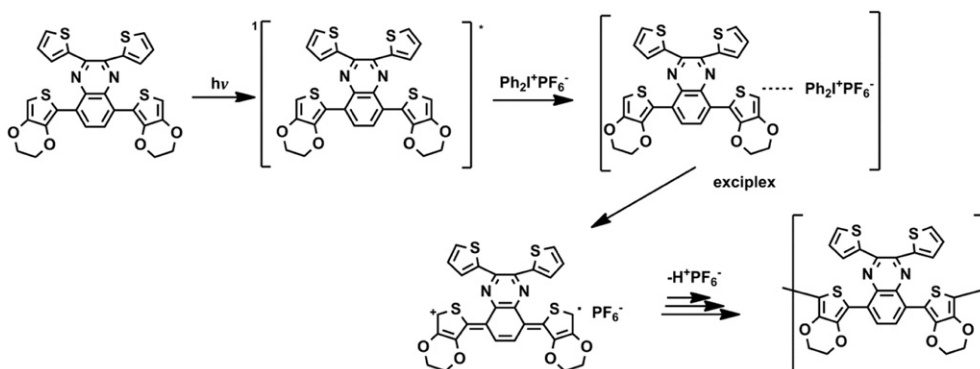
### 2.3. Characterization

The kinetic of the photopolymerization was followed by Real-Time FT-IR spectroscopy, employing a Thermo-Nicolet 5700 instrument. The formulations were coated onto a silicon wafer with a thickness of 50 μm. The samples were exposed simultaneously to the UV beam, which induces the polymerization, and to the IR beam, which analyzes the extent of the reaction. Because the IR absorbance is proportional to the monomer concentration, conversion versus irradiation time profiles can be obtained. Epoxy conversion was followed by monitoring the decrease in the absorbance of the typical epoxy peak centered at 760 cm<sup>-1</sup>. A medium pressure mercury lamp equipped with an optical guide (Hamamatsu LC8) was used to induce the photopolymerization. The light intensity on the surface of the sample was about 50 mW/cm<sup>2</sup>.

Electrical properties of the cured films have been tested with a particular setup, featuring a 4-point probe geometry obtained by shadow masking and high vacuum thermal evaporation of Ti (20 nm, adhesion promoter)/Au (200 nm, conduction layer) over the glass and below the nanocomposite. The cured resin is in electrical contact with the underlying electrodes; since the measured resistance is quite high, only 2 electrodes are used in the samples here compared. Standard I-V measurements have been done at room temperature, letting the sample relax with a repetition of non-consecutive measures; resistivity is determined measuring the sample size and the slope of the linear fit of the mean between three measures performed over the domain [−50, +50] V.

## 3. Results and discussion

As the conducting polymer precursor, we selected bare thiophene monomer. Because of its insignificant absorption, the iodonium salt absorbs the light efficiently in the UV region. Analogous to the well-established cationic initiation mechanism of



Scheme 1. Photoinduced synthesis highly conjugated polythiophenes.

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