

## Synthesis of silver/epoxy nanocomposites by visible light sensitization using highly conjugated thiophene derivatives

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### ABSTRACT

A novel one-pot photochemical strategy for the preparation of silver–epoxy nanocomposite using a highly conjugated thiophene derivative and silver salt was described. Electron transfer reaction between photoexcited 3,5-bis(4-methoxyphenyl)dithieno[3,2-b;2,3-d]thiophene, (P-DDT) and silver salt could be achieved under visible light irradiation. The polymerization process has been demonstrated to be highly efficient in the concomitant cationic ring-opening polymerization of epoxy ring and silver ion reduction. The produced nanocomposite contains spherical shaped nanoparticles homogeneously dispersed in the epoxy network with narrow size distribution in between 25 and 50 nm.

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### 1. Introduction

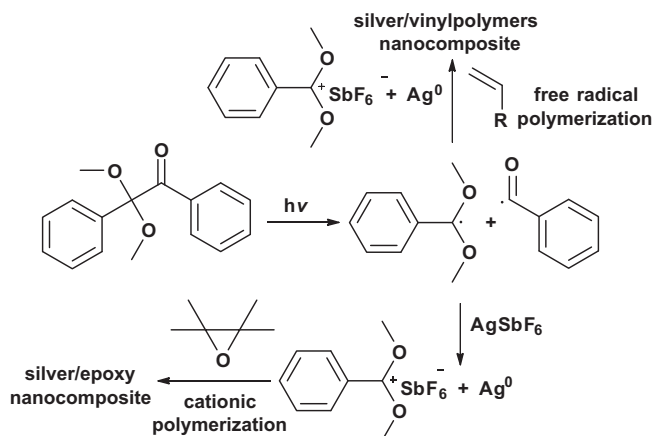
Over past decade, synthetic routes to produce nanoparticles with selective size and shape have become an important research field in materials science [1,2]. In particular, the size-dependent optical and electronic properties have promoted the emergence of extensive applications in various fields [3–6]. Nanocomposite materials, which combine the properties of polymers with those of silver nanoparticles such as excellent electrical conductivity [7], anti-microbial [8] and optical properties [9] are considered to be promising systems for advanced functional applications [10]. Typically, core–shell type silver nanocomposites were shown to exhibit superior performance as coaxial nanocables [11], nanocircuits [6] and nanosensors [5]. Silver nanocomposites can be prepared by reductive processes in homogeneous or micellar solution or in preformed polymer films. Typical examples of polymer silver nanocomposites [12] include, but are not limited, polyvinyl alcohol [13], polyimide [14], polystyrene [15], and epoxy and acrylate based networks [16–22]. The commonly encountered drawback of these nanocomposites is the tendency of the nanoparticles to agglomerate arising from their high surface reactivity thereby leading to poor mechanical properties. Most of the useful approaches that provide the homogeneous dispersion of these thermodynamically unstable nanoparticles in the polymer matrix

are based on their stabilization by inert additives. Alternative thermal and photochemical methods involving simultaneous reduction and polymerization processes have been subject of recent interest. Despite the many potential applications, there are still limitations in applying direct excitation of metal salts or complexes for the photochemical preparation of nanocomposites. Specifically, some transparency to high-energy radiation and stability against extensive photochemical degradation are often difficult to achieve [23]. To overcome these issues, we have recently reported a novel approach for the preparation silver [18,20] or gold [24,25] nanocomposites through simultaneous photoinduced electron transfer and polymerization processes. In these cases, some of the photochemically generated radicals initiate the polymerization of olefinic monomers while the others, particularly those possessing electron donating substituents, serve as reducing agent for the precursor metal salt. Monomers with epoxy functionalities that are polymerizable by a cationic mechanism have also been tested. Providing that the precursor salt equipped with non-nucleophilic counter anions, successful polymerization was ensued through the cations formed from the oxidation of electron donor radicals. The overall processes described for both free radical and cationic systems using 2, 2-dimethoxy-2-phenylacetophenone as typical free radical photoinitiator is presented in Scheme 1.

A wide range of polynuclear aromatic compounds such as anthracene, perylene and phenothiazine are known to photosensitize the initiation of cationic polymerization using onium salts [26–32]. Recently, we have reported [33] that a polynuclear thiophene derivative, namely 3,5-diphenyldithieno[3,2-b;2,3-d]-thiophene (DDT), can act as an electron-transfer photosensitizer for diaryliodonium salt cationic photoinitiators. DDT provides good sensitivity in the

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**Scheme 1.** Silver/polymer nanocomposites by photoinduced free radical and free radical promoted cationic polymerization mechanisms.

near UV and visible region. Polymerizations of cyclic ethers and vinyl monomers were readily induced by electron transfer between excited DDT and iodonium ion. By virtue of the thiophene-type radical cation formation and the crucial role of these species in the electropolymerization, the described photoinduced process was also applied to the step-growth polymerization of DDT itself to form conjugated polymers [34]. Inspired by these previously reported photosensitization reactions, we envisioned that electron transfer reaction between photoexcited 3,5-bis(4-methoxyphenyl)dithieno[3,2-b;2,3-d]thiophene, (P-DDT) [35,36] and silver salt could be achieved under visible light irradiation. Herein, we describe the P-DDT photosensitized in situ preparation of silver epoxy nanocomposites. The overall photopolymerization process has been investigated and the cured films are characterized.

## 2. Experimental

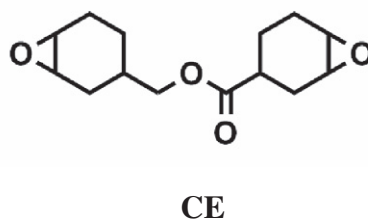
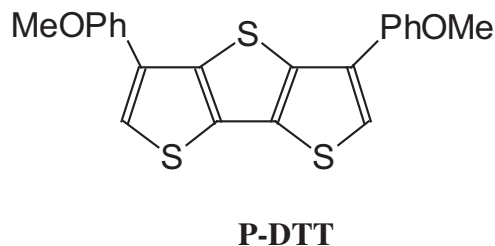
### 2.1. Materials

The thiophene compound, 3,5-bis(4-methoxyphenyl)dithieno[3,2-b;2,3-d]thiophene, (P-DDT), was synthesized according to the previously reported procedure [35]. The epoxy resin 3,4-epoxycyclohexylmethyl 3,4-epoxycyclohexanecarboxylate (EEC) (Aldrich) silver hexafluoroantimonate (Aldrich) were used as received. The schematic structures of the chemicals employed are reported in Table 1.

### 2.2. Sample preparation and photoinduced curing

The silver salt was added to the epoxy resin in the range between 1 and 3 wt.%. The photosensitizer P-DDT was added at 1 and 2 wt.% to the epoxy resin. The different formulations were

**Table 1**  
Chemical structures of the materials employed.



stirred, coated on glass slide and cured with blue light. An Astralis 5 gun lamp was employed to induce photocuring.

### 2.3. Characterization

The kinetics of the photopolymerization was determined by Real-Time FT-IR spectroscopy, employing a Thermo-Nicolet 5700. The formulations were coated onto a silicon wafer. The sample was exposed simultaneously to the visible light, which induces the polymerization, and to the IR beam, which analyze in situ the extent of the reaction. Because the IR absorbance is proportional to the monomer concentration, conversion vs. irradiation time profiles can be obtained. Epoxy group conversion was followed by monitoring the decrease in the absorbance due to epoxy groups in the region 760–780  $\text{cm}^{-1}$ .

An Astralis 5 gun lamp was employed to induce photocuring. Variation in the experimental conditions (light intensity, humidity, temperature) caused slight differences in the kinetic curves. For this reasons all the conversion curves contained in a figure were performed on the same day and under the same conditions; the results are the average of up to 5 runs per each formulation investigated.

The Gel Content was determined on the cured films by measuring the weight loss after 24 h extraction with chloroform at room temperature, according to the standard test method ASTM D2765-84.

Dynamic mechanical thermal analyses (DMTA) were performed with a Rheometric Scientific MKIII (UK) instrument, at a frequency of 1 Hz in the tensile configuration.

The morphology of the obtained materials was investigated by means of a Field Emission Scanning Electron Microscopy (FESEM, Supra 40 Zeiss). The surface fractures of the cured coatings were observed with the In-Lens detector. This detector is an ideal tool to investigate polymeric materials thanks to its high detection efficiency at very low acceleration voltages and the almost pure detection of SE electrons. The detector is placed above the objective lens and detects directly the beam path. The lower the energy of the primary electrons, the smaller the interaction volume and the penetration depth of the electrons will be. The smaller penetration depth of the electrons the higher the share of SE electrons generated in the upper layers of the specimen, which contribute to the image contrast and resolution. This detector allows to collect images at very low acceleration voltages (1.5–5 kV) with the minimization and compensation of the effects due to the accumulation of local charges on the surface of non-conductive materials, that otherwise can significantly deteriorate the imaging quality.

## 3. Results and discussion

The process for preparing nanocomposite was simple and involved several steps, namely photosensitization of P-DDT, formation

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