

New Approach to Chemical Functionalization of Poly(2-chloroxylylene) Thin Films

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ABSTRACT: 3-(8-Octenyl)thiophene was used for successful preparation of functionalized poly-(2-chloroxylylene) (PCX) layers in the course of CVD process. The set of spectral methods used has allowed us to conclude that such modification is based on the chemical reaction of double bonds with xylylene radicals. Functionalized films were used for further chemical transformation in the

course of polycondensation of 3-octylthiophene. Resulted samples are bilayer films and polythiophene layer is chemically connected with PCX one. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 1528–1531, 2011

Key words: film; parylene; thiophene; surface modification; nanocomposites

INTRODUCTION

Polymeric surfaces are hard to be modified since they are relatively inert, possessing few surface reactive groups and a low surface free energy. To improve polymer adhesion and introduce useful functionality, a numbers of chemical processes have been developed. These processes may be grouped as either dry, e.g., in a vacuum system, or wet, as in the use of solvents.

The dry methods typically use an arc discharge or a microwave plasma with various chemicals, i.e., H₂O,^{1–4} NH₃,² Na₂S,⁵ etc. Solution-connected processes usually use aggressive oxidizing reagents, such as H₂CrO₄/H₂SO₄,⁶ fuming H₂SO₄,⁷ etc. The primary drawback of both the wet and dry methods is their tendency to modify not only the polymer surface but also the underlying polymer subsurface, often inducing bond cleavage.

Chemical vapor deposition (CVD) of *cyclo*-di-2-chloro-1,4-xylylene to yield poly-(2-chloroxylylene) (PCX, Parylene C) is an inherently clean process since the monomer gas is directly converted to polymer without the need for initiator or catalysts and produces linear high molecular weight polymer (and thereby good mechanical properties and good transparency). It has gained substantial interest in recent years since it proceeds in the absence of solvents and produces conformal pinhole free coatings,

regardless of the geometric complexity of the substrate. The coatings obtained demonstrate excellent barrier properties, low dielectric constant, and high solvent resistance. They have found applications in circuit boards, semiconductors, hybrid circuits, corrosion resistant coatings, and biocompatible coatings.⁸

PCX is a semicrystalline polymer with degrees of crystallinity and crystalline modifications that are dependent on the deposition conditions.⁹ The crystalline domains of PCX are embedded in an amorphous matrix and are responsible for its chemical and solvent resistance. The incorporation of chemically reactive functional groups to PCX thin-film coatings to produce surface engineering templates has been a subject of considerable interest.

We report here new variant of implementation of our approach to chemical surface modification of PCX films as an alternative method for the production of functionalized PCX coatings. This approach relies on the SOLID technology to deposit PCX films directly over liquid substrates.^{10,11} Our first publication was devoted to the functionalization of PCX through reactions with organic and polymeric compounds bearing double bond(s) in combination with fluorene fragments, which are responsible for novel photophysical properties of materials obtained.¹² In this work thiophene fragment was chemically linked with parylene film and then used as a comonomer in the course of poly-(3-octylthiophene) oxidative polycondensation.

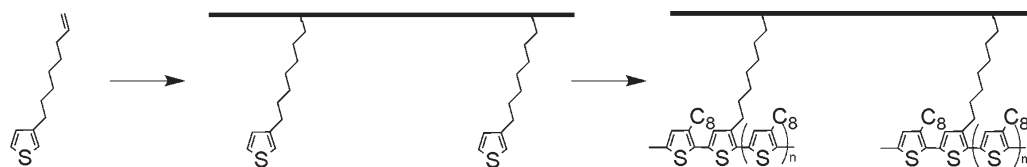
EXPERIMENTAL

Instrumentation and measurements

IR measurements were performed on a Bruker Tensor 27, while the UV-Vis spectra were recorded with

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Scheme 1 Sequence of transformations performed in this work.

a Lambda 900 Perkin–Elmer Spectrophotometer. Images were collected with a Nikon Eclipse TE2000-U inverted confocal microscope with a long working distance and using a Plan Fluor objective (magnification 40, N.A. 0.75).

Materials

Most of the reagents were supplied by Aldrich and used without further purification. *Cyclo*-di-2-chloro-1,4-xylene was obtained from Galentis Srl. and purified by sublimation before polymerization. Synthesis of 3-(8-octenyl)thiophene (OT) was performed according to a method that was published by Hong et. al.¹³

Preparation of composites with PCX by CVD process

The idea of our approach is shown in Scheme 1.

PCX was synthesized from *cyclo*-di-2-chloro-1,4-xylene according to the Gorham process¹⁴ on the surface of OT drop. Additional details could be found in Ref. 10. Free-standing films of composites were obtained by peeling the polymeric film off the substrate. Samples of thickness ranging from 1 to 4 μm were extracted in Soxhlet apparatus with hot CHCl_3 for 48 h. Transparent colorless film (PCX-OT) similar to pure PCX film was obtained.

Synthesis of poly(3-octylthiophene) (POT) in the presence of PCX-OT

Two pieces of PCX-OT film (of ca. 2×3 cm each) took part in chemical oxidation of 3-octylthiophene with anhydrous FeCl_3 in chloroform.¹⁵ After oxidation reaction, films were washed with chloroform, ethanol with NH_4OH , acetone and then extracted for 36 hrs with chloroform until obtaining two yellowish-brown samples. General view of this composite of PCX and POT is shown in Scheme 1. Polymer formed in the reaction mixture (not connected with PCX films) was collected, washed with ethanol and acetone. This is very dark brown-reddish solid.

RESULTS AND DISCUSSION

General considerations

The radical polymerization of PCX takes place just in the upper layer of a medium that is best

described as a slightly swollen, solid polymer.¹⁶ We believe that thiophene is, however, available for further chemical reaction of the surface of composite. This peculiarity of PCX growth was used for interaction with double or triple bonds of various organic molecules and polymers.¹² The idea of current investigation was chemically modify PCX surface with 3-(8-octenyl)thiophene and then include linked alkylthiophene molecules into chains of growing poly(3-octylthiophene) (POT).

Characterization of PCX-OT composite

UV-vis spectra of PCX-OT and neat PCX are very similar due to low concentration of thiophene rings and weak absorption of this compound.

FTIR spectra of initial compounds and composite are shown in Figure 1. Spectrum of OT demonstrate bands typical for $-\text{CH}=\text{CH}_2$ groups at 910, 993, and 1640 cm^{-1} . In the spectrum of composite all these bands are absent which means that most of them are chemically reacted with parylene molecules (or that the amount of unreacted OT molecules is undetectable by FTIR). The same conclusion could be drawn from comparison of spectra in $3000\text{--}3100\text{ cm}^{-1}$ region-band at 3075 cm^{-1} typical for $-\text{CH}=\text{CH}_2$ group is absent in the composite (not shown).

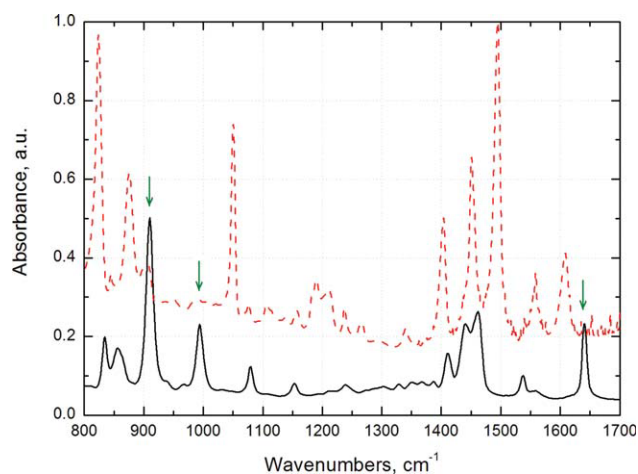


Figure 1 IR spectra ($800\text{--}1700\text{ cm}^{-1}$ region) of OT (black solid) in comparison with PCX-OT (red dash). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

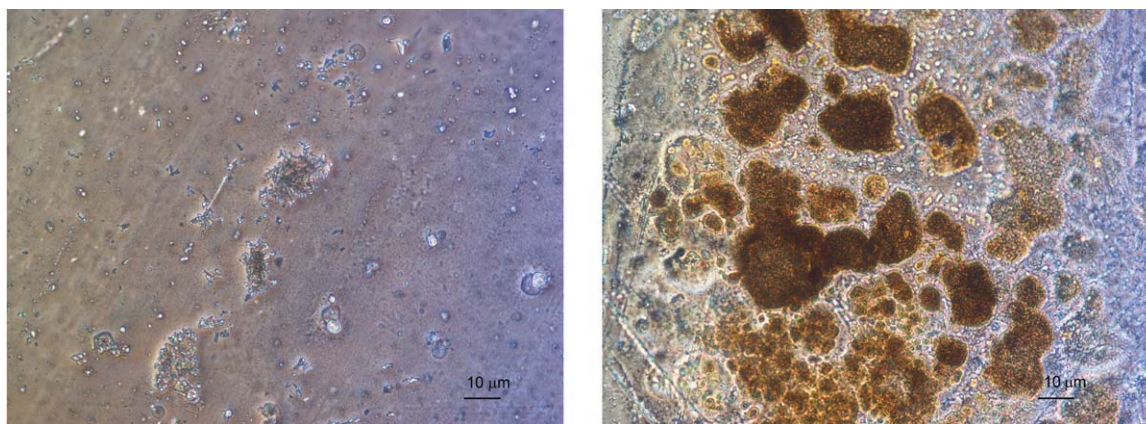


Figure 2 Microphotographs ($\times 20$) of neat Parylene C (left) and PCX-OT/POT (right). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

At the same time the presence of alkylthiophene moieties is evidenced by the 1460 cm^{-1} band which is attributed to the ring breathing of the thiophene.

Synthesis of poly-(3-octylthiophene) in the presence of PCX-OT film

Following the procedure described in experimental part the composite PCX-OT was reacted with 3-octylthiophene. Microphotographs of films obtained are given in Figure 2. Considerable amount of colored substance is present on the PCX-OT/POT film. This substance remains after 36 h extraction with chloroform and can not be removed mechanically (with cotton pad wetted with chloroform).

UV-vis spectrum of product obtained after polycondensation reaction which remains as a powder (Fig. 3, red) is quite similar with library spectrum of POT. Blue shift ($\sim 20\text{ nm}$ from 419 nm characteristic for regiorandom polymer from Sigma-Aldrich) could

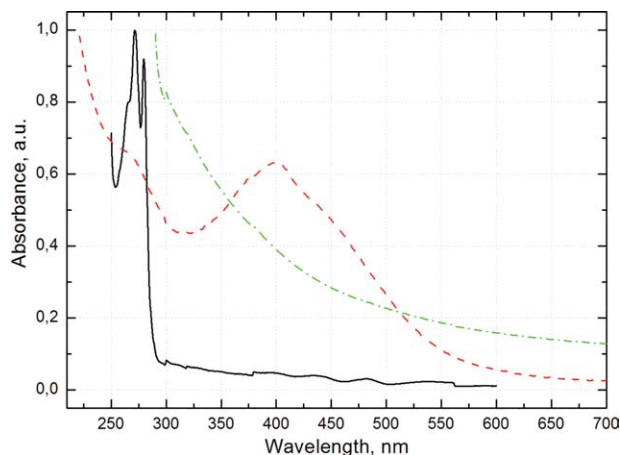


Figure 3 UV-vis spectra of PCX-OT film (black), poly(3-octylthiophene) film on KBr (red) and PCX-OT/P8T (green). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

be connected with low molecular weight of our product.

So, one can conclude, that polymer formed as a result of oxidative polycondensation of octylthiophene is low molecular weight POT.

Characterization of PCX-OT/POT composite

UV-vis spectrum of PCX-OT/POT film doesn't contain a well defined band: it shows a wide distribution of conjugation length of oligomeric and polymeric chains probably connected with PCX (due to additional diffusion and spatial problems in the course of polycondensation reaction).

FTIR spectra of PCX and PCX-OT/POT composite film are given in Figure 4. Note, that the last spectrum (in red color in the figure) was registered against PCX background. In that spectrum of

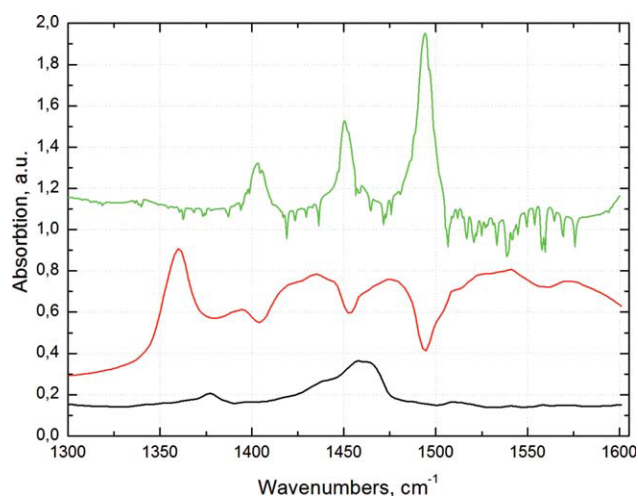


Figure 4 FTIR spectra ($1300\text{--}1600\text{ cm}^{-1}$ region) of POT (black bottom) in comparison with PCX-OT/P8T (red middle; registered against PCX background) and PCX (green top). Spectra are shifted for clarity. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

composite shoulder at 1420 and bands at 1440 and 1475 cm^{-1} appears. These bands are also present in the FTIR spectrum of POT and have been attributed to the ring breathing of the thiophene.

CONCLUSIONS

OT reacts with *p*-xylylene moieties in the course of PCX formation which leads to chemical modification of the surface of film. Chemical oxidation of octylthiophene in the presence of PCX-connected thiophene moieties results in considerable amount of nonsoluble yellow product on the surface. Optical microscopy observations confirm this conclusion. According both UV-vis and FTIR spectroscopy nonsoluble product on the surface is the POT chemically connected (though thiophene moieties of OT fragments) with PCX.

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