# POLY (OLEFIN SULFONE)$_S$ (POS$_S$)/CARBON NANOTUBE COMPOSITES IN SENSORS/BIOSENSORS APPLICATIONS.

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## Abstract

Organic polymers can be used as the active component of sensors and layer of solar cells. Ionizing radiation is radiation capable of ejecting an electron from an atom upon interaction with organic matter. The rational design and modification of the chemical structure of polymers has enabled control over their properties and morphology, leading to the advancement of Nanotechnology. Sensing the presence of ionizing radiation is crucial in several fields, including energy, biological and nuclear research. In general, systems used for the detection and dosimetry of ionizing radiation usually have one or several drawbacks. In this study, we report a new sensing scheme for radiation based on organic materials, in which the signal is not generated by

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*scintillation or charge creation in a semi-conductor. The system herein described is based on the degradation of the radiation labile polymeric matrix of a composite film upon radiation exposure, which leads to large resistivity changes in a composite film. We also show how chemical design and tailoring of the sides chains of this active polymer using an orthogonal post polymerization modification can be used for the optimization of sensor performance. All reactions were performed using standard Schlenk techniques. Poly (Olefin Sulfone) (POS) synthesis was carried out following literature procedures. In order to test these ideas, devices containing a thin film of a poly (1-hexene Sulfone) (P1HS) and multi-walled carbon nanotubes (MWCNTs) were fabricated. When the current measured under a constant potential of devices fabricated with different ratios of P1HS to MWCNTs was investigated, it was evidenced that increasing loadings of P1HS yielded Lower Conductivities for the composite films. The chemical structure of the active element in the sensor was modified to improve device sensitivity.*

## INTRODUCTION

Ionizing radiation is radiation capable of ejecting an electron from an atom upon interaction with matter.[3] There are several types of ionizing radiation and they differ from each other depending on the mass and on their charge.[1] The degree of ionization, and the mechanisms by which ionization occurs are highly dependent on the nature of the ionizing radiation, and the composition of the matter being irradiated.[2] Charged radiation will tend to induce a higher degree of ionization as these charges interact strongly with the electrons to be ejected, and matter composed of heavier elements tends to interact more with high energy photons, as each atom contains more electrons.[4]

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Sensing the presence of ionizing radiation is crucial in several fields, including energy, biological and nuclear research.[5] In all these situations, it becomes necessary not only to sense the presence of ionizing radiation, but also to quantify the cumulative doses of radiation absorbed over time using a dosimeter.[7] this is interesting from the point of view of personal protection, as well as monitoring materials attrition.

Dosimeter design usually involves a sensing event, in which the sensor undergoes an irreversible modification.[8] This is the case for the most commonly used system for personal dosimetry of radiation, which is based on the development of a photographic film.[10] in general, systems used for the detection and dosimetry of ionizing radiation usually have one or several of the following drawbacks: Incapability to produce a real-time signal; expensive and/or complicated manufacturing like on CdZnTe based systems, low sensitivity to non-charged radiation which is particularly problematic for systems based on organic materials; a voluminous size like the Geiger counter; and relatively high fragility like for the case of smaller systems based in the ionization of a gas trapped inside a chamber.[12]

In this study, we report a new sensing scheme for radiation based on organic materials, in which the signal is not generated by Scintillation or charge creation in a semiconductor. The system herein described is based on the degradation of the radiation labile polymeric matrix of a composite film upon radiation exposure, which leads to large resistivity changes in a composite film.[11] we also show how chemical design and tailoring of the side chains of this active polymer using an orthogonal post polymerization modification can be used for the optimization of sensor performance, namely to influence the sensitivity of the resulting materials towards radiations.[9]

The proposed sensor is an irreversible sensor that could be used for dosimetry of high energy photons. The active component of this

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sensor is a thin composite film consisting of two elements: (a) poly (1-hexene Sulfone) (P1HS), which is a non-conducting polymeric matrix capable of degrading in the presence of radiation leading to deploymerization and generation of volatile monomers which can in turn escape from the film. (b) Carbon nanotubes (CNTs) which is a semiconducting element with a high aspect ratio. Poly (Olefin Sulfone)s (POS)s; are Sulfur dioxide ($SO_2$)/Olefin copolymers which have relatively low ceiling temperatures and degrade in the presence of ionizing radiation (high energy electrons) [11]. Due to this fact, they are used as electron beam resists in electron beams Lithography.[12] POSs were first reported in 1898, when Russian Chemist Solonina First mixed Liquid Sulfur dioxide and an Olefin in the presence of a radical initiator to obtain an unidentified white powder.[8] It was not until Staudinger developed his macromolecular theory that this initial white powder was correctly identified as a polymer [10]. POSs, can be readily obtained in industrial scale and they exhibit good mechanical properties, which are tunable depending on the Olefin of choice.[4] However, they have not been more extensively deployed as commodity polymers due to their tendency to degrade under certain conditions.[8]

Carbon Nanotubes (CNTs) are carbon based materials that show unique mechanical and electronic properties ranging from semiconducting to metallic depending on their molecular structure. These materials have become readily available in the recent years, which has enabled their modifications and deposition for deployment as sensors, electrodes, super capacitors, catalysts, filters and for organic electronic applications.[7] One of the most important characteristics of carbon nanotubes is their large aspect ratio, due to which they can be considered one dimensional nanowires. It is worth noting that since these materials are carbon based, they are also

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relatively cheap and light. For these reasons, they were the materials of choice as the semi-conducting element in the sensing scheme.[6]

## MATERIALS AND METHODS

**Materials:** All reactions were performed in flame dried glassware, and under an oxygen free atmosphere of argon using standard Schlenk techniques. Graduated flasks were used for polymerization reactions with condensed Sulphur dioxide. Anhydrous solvents were obtained using a solvent purification solvent (innovative technologies). Carbon nanotubes were the materials of choice as the semi-conducting element in the sensing scheme. All other chemicals were of reagent grade from sigma Aldrich and were used as received.

**POS Synthesis:** POLY (Olefin Sulfone) (POS) synthesis was carried out following literature procedures. In general, Sulfur dioxide (6ml) was condensed into a graduated vessel at $-78^{\circ}C$. The reaction vessel was then transferred into $-45^{\circ}C$ bath. Olefin monomers were added to the reaction mixture in the desired ratio, and the solution was stirred for 5 minutes. Initiator for the polymerization (tert-Butyl hydroperoxide in decane, solution 5.0-6.0M, 5-10 Mol % relative to total amount of Olefin) was added and the mixture was stirred at $-45^{\circ}C$ for 2 hours. The polymerization was stopped by pouring the reaction mixture into MeOH. The resulting white powder was redissolved in $CHCL_3$ and reprcipitated from MeOH, then wash with MeOH. The white solid obtained was dried under vacuum. 98% yield of POS obtained.

## Synthesis and modification of side-chain functionalized poly (Olefin Sulfone)s:

Azide-containing Olefins were synthesized and successfully incorporated into POSs. In order to attach different functional groups and test the performance of these new POSs, a modular approach was taken, in which a parent polymer with versatile functional groups

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susceptible of undergoing orthogonal chemistry was synthesized, and then functional groups were attached in a post-polymerization modification. (polymerization of 6-azido-1-hexene (obtained from 6-bromo-1-hexene) with $So_2$ and 1-hexene afforded a family of random monomodal terpolymers, azide-POS (see the equation below). The actual loading of azide on the side chain (defined as the molar fraction of repeat unit containing azides on the side chains, $X_b$ versus the molar ratio of repeat unit containing unfunctionalized side-chains, $x_a$) was traced by $^1$H-NMR and infrared (IR) spectroscopic techniques (figure 1 and figure 2 respectively).



**Equation 1: Cu-ca**
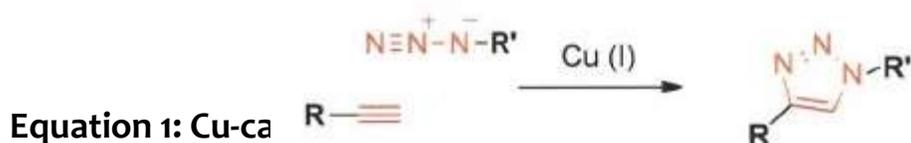
The amount of azido-Olefin incorporated into the final polymer ($X_b$) was proportional to the amount in the initial feed ($X_B$) as shown in figure 3. This allows for perfect control over the loading of azide functionalities on the side chain of the polymer. Post-polymerization of Huisgen 1,3-dipolar cycloaddition with alkynyl molecules provided these azide-POSs with the desired functionality.

**Ionizing Radiation Detection**
In order to test these ideas, devices containing a thin film of a Poly (1-hexene Sulfone) (P1HS) and multi-walled carbon Nanotubes (MWCNTs) (figure 4) were fabricated. Thin film of these composites were drop-cast on an inert substrate (glass), and gold electrodes were deposited on top (as illustrated in figure 5).
When the current measured, under a constant potential of devices fabricated with different ratios of P1HS to MWCNTs was investigated,

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it was evidenced that increasing loadings of P1HS yielded lower conductivities for the composite films. This was expected, since a lower ratio of MWCNTs to P1HS means a higher degree of separation of the MWCNTs in the blend (figure 6).

When an array of devices of radiation were exposed to high doses of radiation ($5x10^6$ rad), an increase in the conductivity of up to 103-fold as compared to a non-irradiated reference of the same composition (fig 7) was observed. This increase was larger for lower starting conductivities. As expected, when the matrix degrades, carbon nanotubes come into contact creating conducting pathways, which lead to higher overall conductivities.

Degradation of the polymeric matrix (P1HS) was seen by optical microscope. After irradiated, bubbles (pores) appears in the films, created by the volatile monomers generated after ionization and unizipping the polymer chains.

When organic matrices other than P1HS were used, the results were different. These results are summarized in figure 8. Only when radiation labile polymers, traditionally used as electron beam such as POSs and Poly (methyl methacrylate) (PMMA) are used, an increase in the conductivity was seen. When more radiation robust polymer such as Poly (Styrene) (PS) was used, no charge in films and in the device signal was observed. The same was observed when small molecule analogues of POSs, such as 3-Sulfolene was used as the matrix. Even though 3-Sulfolene has also been reported to degrade in the presence of ionizing radiation, going back to butadiene and Sulfur dioxide, this was an isolated event with no amplification. In the case of POSs, one bond cleavage event leads to unzipping of the whole polymer chain (amplification), which in turn leads to significant changes in the morphology.

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## RESULTS

## FIG 1: ¹H-NMR spectra for POS with different ratios
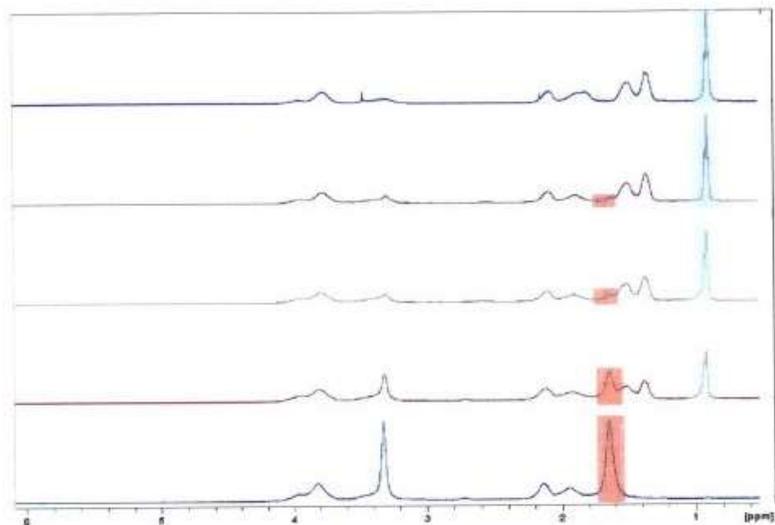


## FIG 2: IR Spectra of POS with different of ratios

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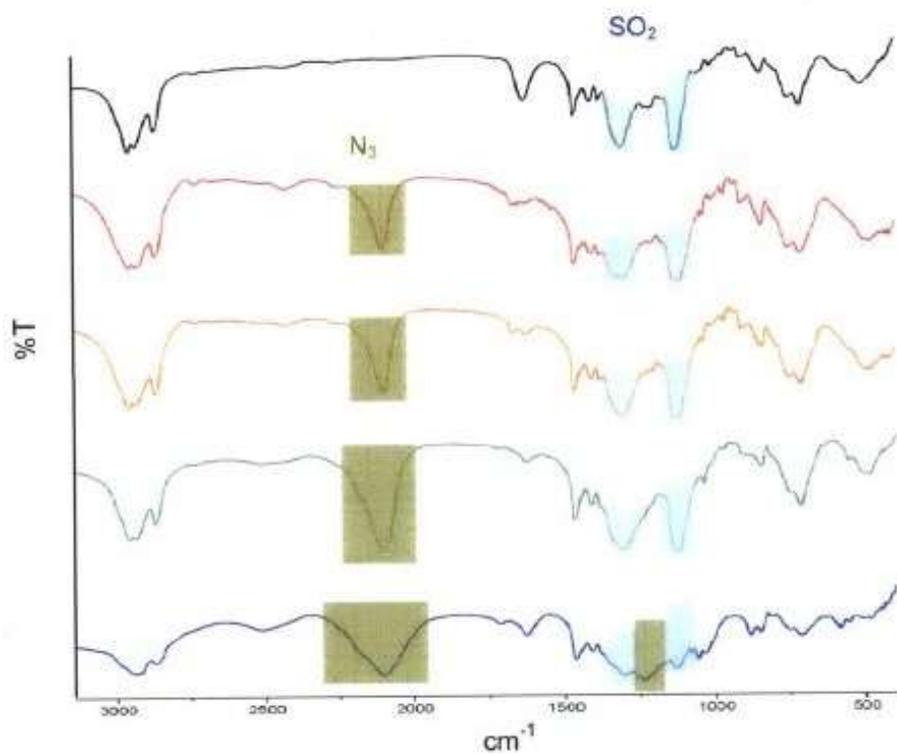
**FIG 3: Molar ratios of 6-azido-1-hexene ($X_B$) in the feed vs. molar ratio of repeat unit containing azide monomer ($X_b$), as determined by ¹H NMR spectroscopy**
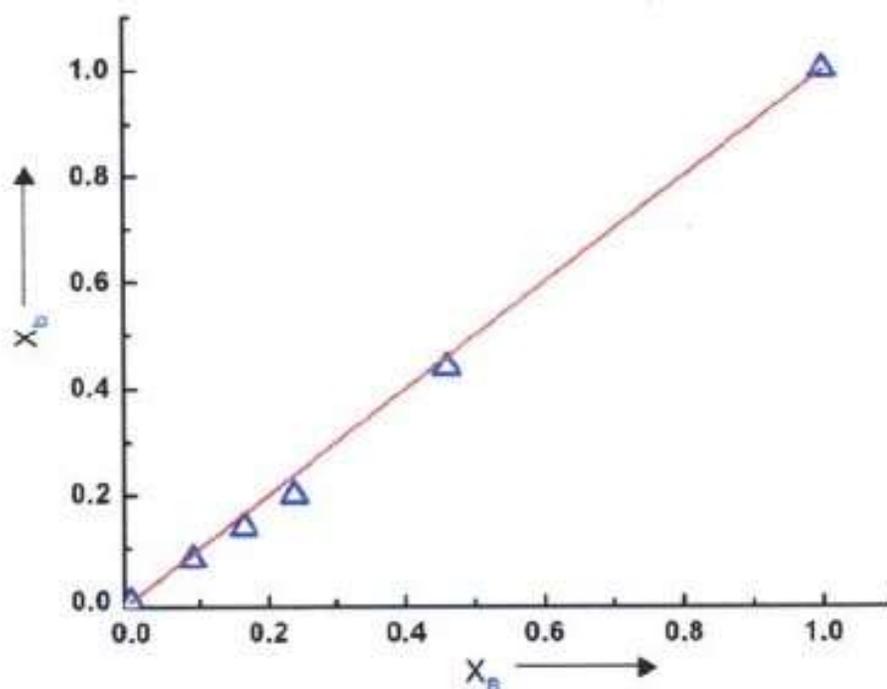


**FIG 4: Structure of Poly (1-hexene sulfone) and schematic representation of MWCNT**

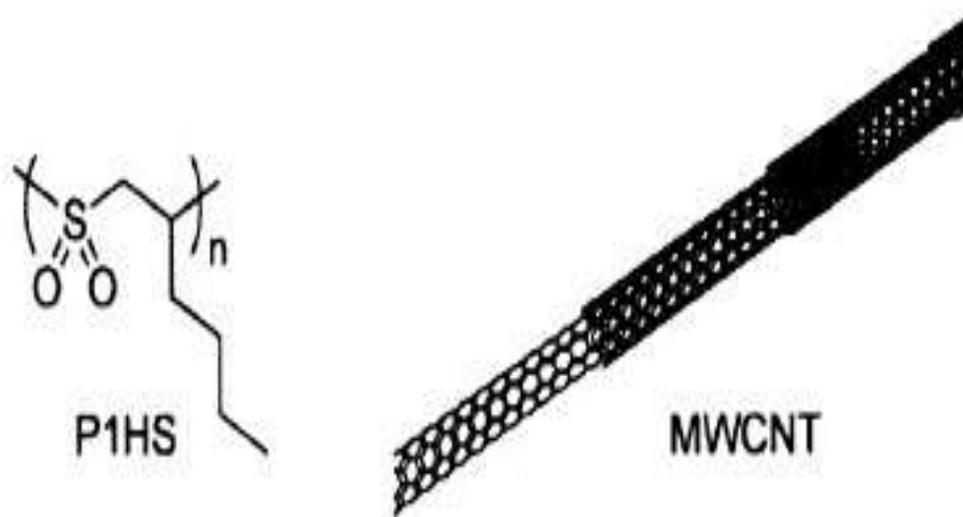**EDITOR-IN-CHIEF**
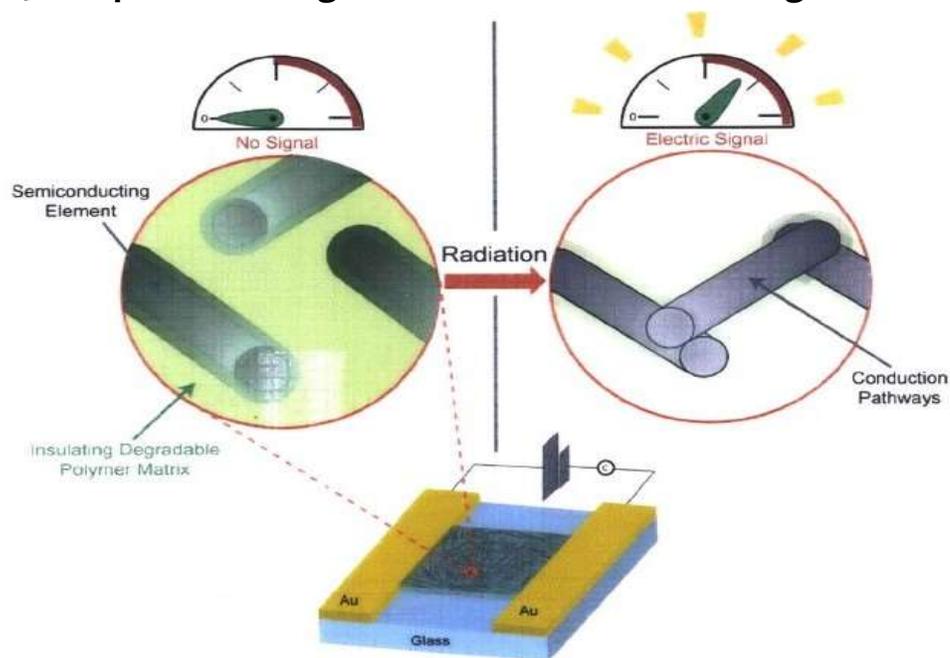**Prof. A.S. Hossein [Saskatchewan]**

**FIG 5: Proposed sensing scheme for radiation sensing.**



**FIG 6: Amperometric measurements (constants voltage IV) for films containing different ratios of P1HS to MWCNTs.**

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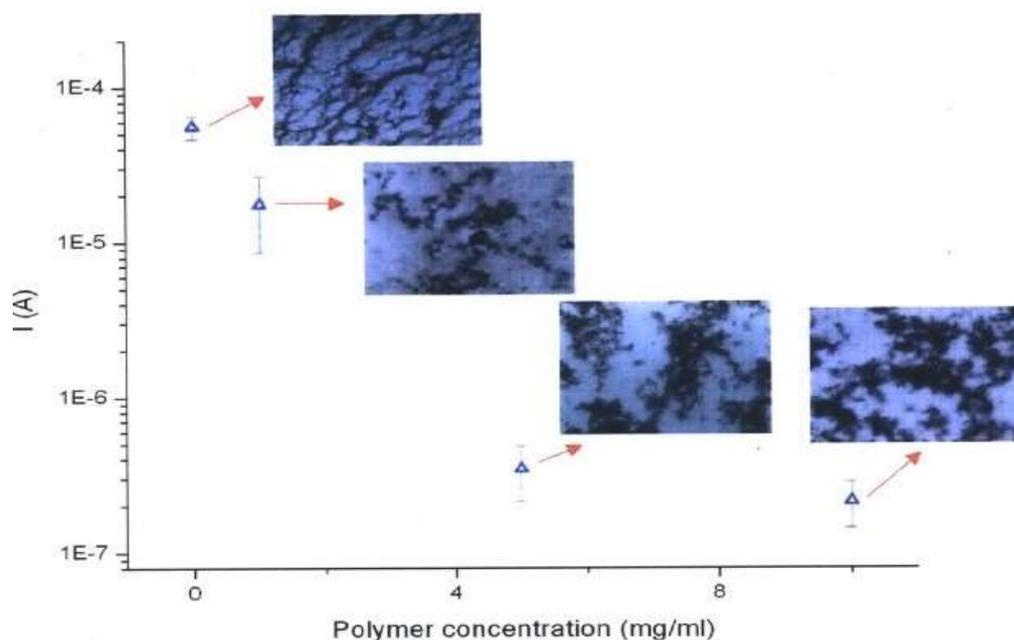**Prof. A.S. Hossein [Saskatchewan]**

**FIG 7: Amperometric measurements over time for devices of equal composition (P1HS/MWCNs) that were not exposed to radiation (left), and that were exposed to radiation (right).**
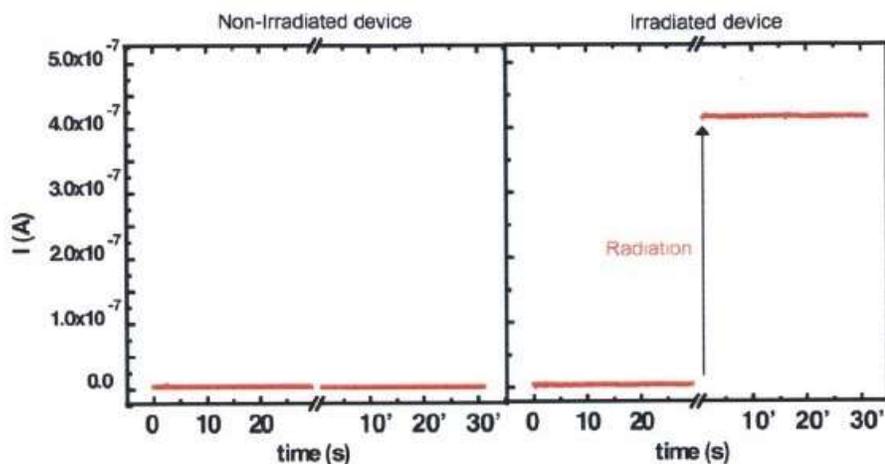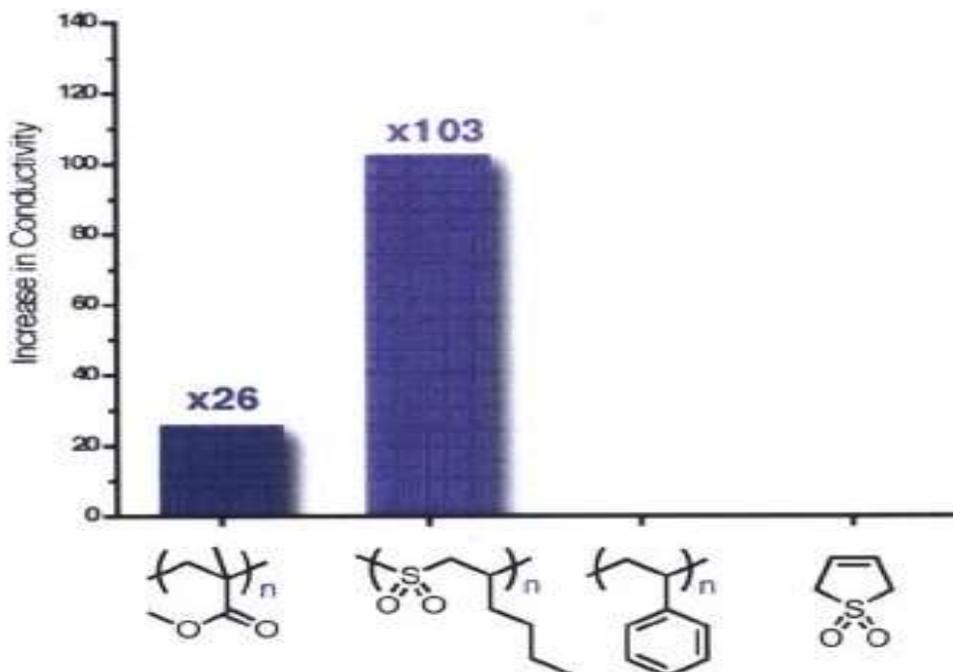


**FIG 8: Increase in conductivity after irradiation (radiation dose: $5 \cdot 10^6$ rad) for devices using different organic matrices (from left to right: PMMA, P1HS, PS and 3-sulfolence) and MWCTs.**

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## DISCUSSION

In this study we have shown how a novel sensing scheme that is not based on Scintillation or charge generation in semi-conductors can be deployed for the detection of uncharged ionization radiation using small devices. Our sensing mechanism makes use of a polymer/multiwalled carbon nanotubes (MWCNT) blend as the active layer of small devices for detection of radiations. This system is capable of producing a real-time signal at room temperature, composed of relatively inexpensive starting materials, with nearly zero cost of operation.

In this system, the conducting MWCNTs form a percolated network and are partially isolated from each other in a non-conductive polymeric matrix. The turn-on detection mechanism is as follows: upon irradiation of the composite, matrix, creating a lower resistance connection between the MWCNTs. The depolymerization creates amplification and large changes in the electrical properties of the composite, increasing its conductivity. Functional POSs were accessed by Click Chemistry methods, and several strategies were successfully deployed to increase sensor sensitivity. We have shown that systematic improvements in sensitivity can be accomplished by rational design, and incorporation of the appropriate chemical components to achieve sensitivities in the $10^3$ rad range.[12] This is a good example of how rational design and chemical modification can lead to large changes in materials performance.

When comparing P1HS and PMMA as a matrix, the sensitivity of devices is much higher for the case of P1HS. This is due to the fact that P1HS has a much higher tendency to degrade in the presence of ionizing radiation, which leads to larger changes in the morphology.

To test the dynamic range of the detectors, a lower dose of $5 \times 10^3$ rad was employed, and devices also showed a detectable increase in the conductivity as compared to a non-irradiated, reference. However, the

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conductivity was at the lower detection unit of the amperometer used, and devices failed to show a response when exposed to even lower doses. The lack of signal at lower doses is mainly due to one problem: The initial homogeneity of the films was very poor, owing to the lack of favourable interactions between the POS and the CNTs. Large CNT aggregates was observed, and this is detrimental for sensor performance.

In order to address this concern, and to improve device sensitivity, we decided to modify the chemical structure of the active element in the sensor. For this purpose, we embarked on the synthesis of POSs containing functional groups on the side chains.

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