

Radiation Detection: Resistivity Responses in Functional Poly(Olefin Sulfone)/Carbon Nanotube Composites**

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Detection and dosimetry of ionizing radiation^[1] are crucial in several fields such as energy, national security, biological and nuclear research, and in other advanced applications such as monitoring the attrition of materials in space travel. The most common systems for the detection and dosimetry of ionizing radiation usually have one or several of the following drawbacks: incapability to produce a real-time signal,^[2] expensive and/or complicated manufacturing,^[3] need for operation at low temperatures,^[4] low sensitivity to non-charged radiation,^[5] or voluminous size.^[6]

Although organic materials present the advantages of being easily processed, synthetic versatility, and relatively low cost, deployment of organic systems as small-size ionizing radiation detectors and dosimeters has been traditionally limited to the detection of charged particles, owing to the low gamma ray cross sections of elements incorporated in these molecules.^[7]

We report herein a new sensing scheme that is not based on scintillation or charge generation in semiconductors. Our sensing mechanism (Figure 1) makes use of a polymer/multiwalled carbon nanotube (MWCNT) blend for the detection of gamma rays, capable of producing a real-time signal at room temperature, composed of relatively inexpensive starting materials, with nearly zero cost of operation and a small size. In our 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, ionization induces depolymerization of the 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, which can be detected by amperometry (measurement over time of the current intensity I between two electrodes at a constant potential V). For the aforementioned sensing scheme to work, the following requirements need to be met: a) the polymer must degrade rapidly upon ionization, b) the MWCNTs must be initially well dispersed in the

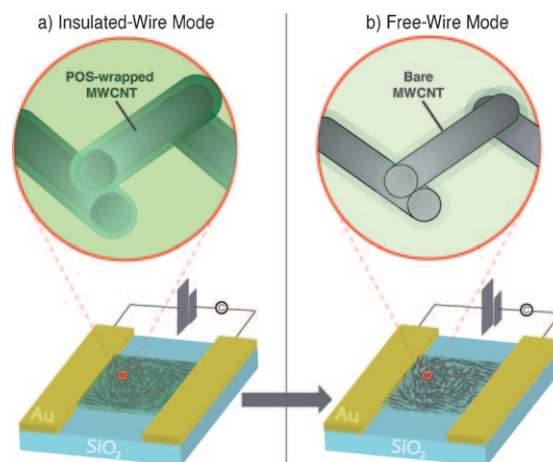
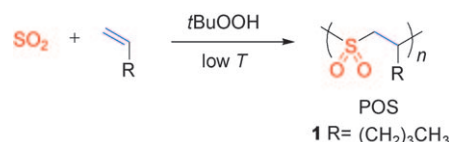


Figure 1. Sensor design showing a) a low conductance device where the CNTs are wrapped with non-conducting POS, which upon ionization develops b) interconnected nanocircuitry and a higher conductance.

polymeric matrix, and c) the system must have a high radiation harvesting yield and ease of ionization.

We have selected poly(olefin sulfone)s (POSs; Scheme 1) as our polymer matrix; poly(1-hexene sulfone) (**1**) degrades in the presence of ionizing radiation (high energy electrons,^[8]



Scheme 1. Synthesis of poly(olefin sulfone)s (POSs).

gamma rays),^[8,9] and is used as an electron beam resist.^[8,10] Irradiation induces chain-scission and depolymerization,^[11] releasing sulfur dioxide (SO_2) gas and a volatile olefin.^[12] These polymers are synthesized by radical chain growth polymerization of SO_2 and the olefin. Standard synthetic conditions involve bulk polymerization at low temperatures with condensed liquid SO_2 as the solvent and *tert*-butyl hydroperoxide as the initiator.^[12] Polymers obtained in this manner usually show a 1:1 ratio of perfectly alternating sulfone and olefin units when there is an alkyl moiety directly linked to the olefinic residue.^[10b] Olefins used for these polymerization conditions must be electron-rich, sterically unhindered, non-basic, and display at least moderate solubility in SO_2 .^[10b]

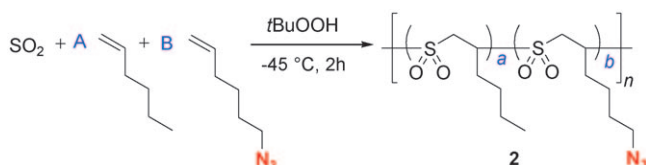
Early studies revealed that unfunctionalized POSs yielded poor dispersions of MWCNTs. In addition, to reach good

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levels of sensitivity, the gamma ray absorption cross section of the POSSs needed to be improved. To fulfil these requirements, functional POSSs were synthesized. Even though monomers with many different functional groups have been successfully incorporated into POSSs,^[13] several restrictions in the monomer choice arise from the nature and conditions of the polymerization process. Given that “click chemistry” has proven to be an extremely useful tool for the post-polymerization functionalization of polymers,^[14] azide-containing olefins were synthesized and successfully incorporated into the main chains of the POSSs. Copolymerization of 6-azido-1-hexene with SO₂ and 1-hexene (Scheme 2) afforded a family



Scheme 2. Synthesis of azide-containing poly(olefin sulfone)s.

of random monomodal terpolymers (**2**) in which the ratio of incorporation of olefin to azido-olefin (*a/b*) was identical to the feed ratio (*A/B*; see Figure 2, ideal azeotropic copoly-

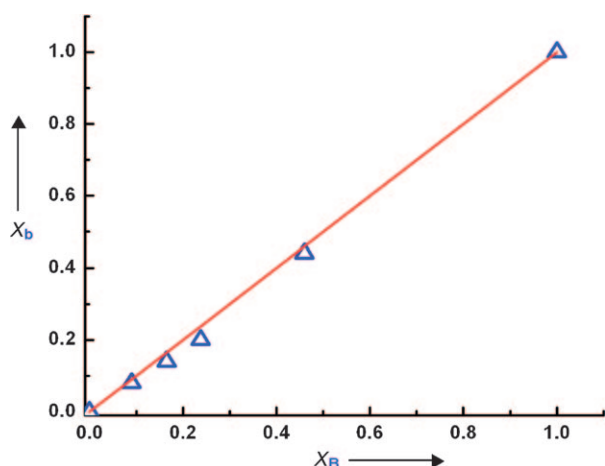
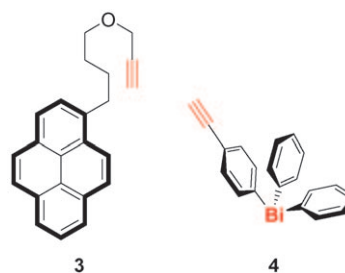


Figure 2. Molar ratio of 6-azido-1-hexene (*X_B*) in the feed (*x* axis) vs. molar ratio of repeat unit containing azide monomer (*X_B*), as determined by ¹H NMR spectroscopy.

merization). This allows for perfect control over the loading of azide functionalities on the side chain of the polymer. Huisgen 1,3-dipolar cycloaddition with alkynyl molecules provided the desired functionality to our POSSs.

To improve the dispersion capabilities of MWCNTs, pyrene was attached to the side chains of our POSSs in order to bind to the surface of MWCNTs by π - π stacking.^[13] This interaction has been used to tailor the surface of CNTs for functionalization purposes, leaving the electronic structure of the tubes intact.^[16] Using click chemistry, pyrene **3** (Scheme 3), was incorporated into the POSSs, leading to a

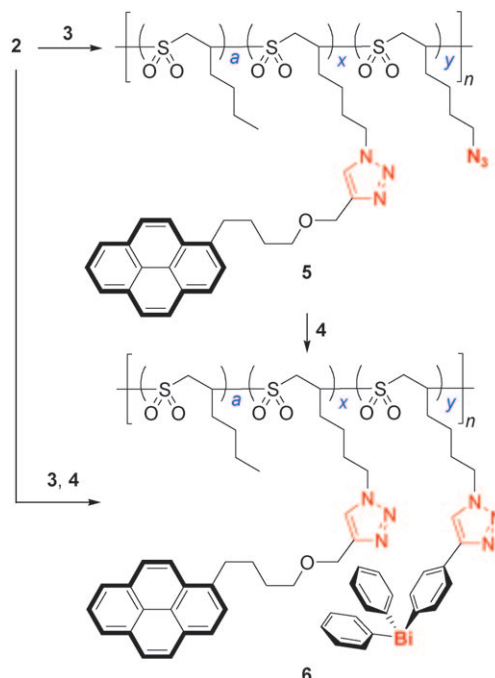


Scheme 3. Alkynyl partners for click chemistry.

better interaction between MWCNTs and POSSs, and consequently, less phase separation.

Cross-section values for ionization caused by gamma rays of different elements increase with increasing *Z* (atomic number).^[7] Bismuth is considered to be the heaviest non-radioactive element in the periodic table,^[17] and doping polymers with Bi has been shown to increase the opacity of the resulting polymers towards ionizing radiation.^[18] Bi complex **4** (Scheme 3) was used for the click reaction. Bismuth loadings as high as 20% (characterized by gel permeation chromatography (GPC), ¹H NMR spectroscopy, and IR spectroscopy) were achieved in this manner without any reduction in solubility.

Stepwise or one-pot click reactions of polymer **2** with pyrene derivative **3** and complex **4** yielded polymer families **5** and **6**, the latter incorporating both pyrene and bismuth functionalities (Scheme 4). The resulting polymers, **5** and **6**, were characterized by GPC, ¹H NMR spectroscopy, and IR spectroscopy. Presence of Bi in **6** was confirmed by X-ray photoelectron spectroscopy (XPS).



Scheme 4. Synthesis of functional POSSs. Conditions for the click reactions: CuBr (10 mol%), sodium ascorbate (15 mol%), *i*Pr₂NEt (10 mol%), DMF, RT, 24 h.

Irradiation of devices composed of a blend of **1** with MWCNTs with high doses of gamma radiation (5×10^6 rad)^[19] yielded an increase in the conductivity of up to 103-fold as compared to a non-irradiated reference of the same composition (Figure 3). To test the dynamic range of the detectors, a

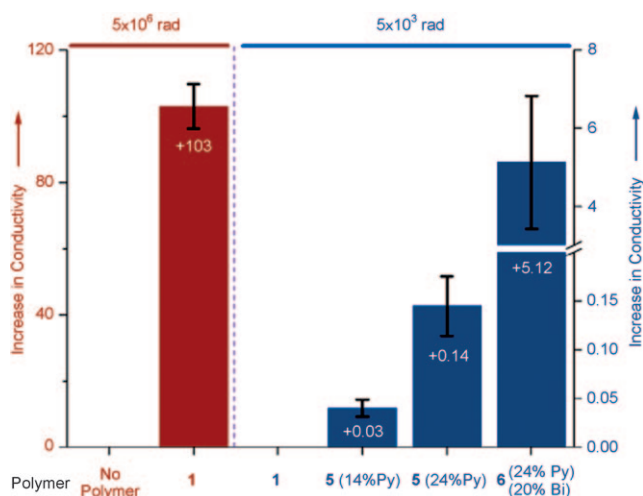


Figure 3. Increase in conductivity (y axis) of irradiated devices fabricated using the specified polymer (x axis) and MWCNTs. Error bars = standard deviation. Two radiation doses were used, 5×10^6 rad (red) and 5×10^3 rad (blue). Better sensitivities were obtained when using functional POSs **5** and **6**.

lower dose of 5×10^3 rad was employed, and devices also showed a detectable increase in the conductivity as compared to a non-irradiated reference. However, the conductivity was at the lower detection limit of our amperometer, and devices failed to show a response when exposed to lower doses. Low sensitivity can be attributed to poor initial dispersion of CNTs in the polymer as revealed by optical microscopy, and to the low gamma ray cross sections of the elements that compose the POS.

When devices fabricated using functional POSs **5** and **6** were exposed to gamma radiation, a more pronounced increase in conductivity was obtained as compared to devices with the unfunctionalized equivalent poly(1-hexene sulfone) (**1**; Figure 3). An increase in the initial homogeneity of the system improved the performance of the devices: if we compare the response of **5** (14 mol% repeat unit x) and **5** (24 mol% repeat unit x) to the same dose of radiation (5×10^3 rad), the signal goes from barely detectable to an increase of about 14%. Incorporation of Bi to increase the opacity of the system towards gamma rays proved to be an even more effective strategy for increasing device response towards radiation: a 5.12-fold increase in the conductivity was detected when using polymer **6** for device fabrication.

In summary, we have shown how a novel sensing scheme that is not based on scintillation or charge generation in semiconductors can be deployed for the detection of uncharged ionization radiation using small devices. Functional POSs were accessed by click chemistry methods, and several strategies were successfully deployed to increase sensor sensitivity. We have shown that systematic improve-

ments in sensitivity can be accomplished by rational design, and incorporation of the appropriate chemical components to achieve sensitivities in the 10^3 rad range.^[20] Further optimization is currently being carried out in our labs for the sensors to operate in a range of lower irradiation doses.

Experimental Section

Detailed experimental procedures and chemical synthesis are described in the Supporting Information. Thin-film deposition on a microscope slide was achieved by drop-casting from a THF solution containing both the POS and commercially available purified CNTs, dispersed by sonication. Gold electrodes were deposited by sputter-coating with a spacing of 1.5 mm between electrodes to enable amperometric measurements. Devices were measured before and after irradiation, and its I (A) signal (variation of I normalized to the initial I) under constant voltage was compared to non-irradiated devices with the same formulation.

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- [1] a) G. F. Knoll in *Radiation Detection and Measurement*, Wiley, New York, **1979**; b) R. H. Herz in *The Photographic Action of Ionizing Radiations*, Wiley-Interscience, London, **1969**.
- [2] For example photographic film badges for dosimetry; see ref. [1b].
- [3] Such as the CdZnTe system; A. Owens, *J. Synchrotron Radiat.* **2006**, *13*, 143–150.
- [4] For example Ge based semiconductor detectors; J. G. Webster in *The Measurement, Sensors and Instrumentation Handbook*, CRC, **1999**, pp. 66–12.
- [5] S. C. Graham, R. H. Friend, S. Fung, S. C. Moratti, *Synth. Met.* **1997**, *84*, 903–904.
- [6] Such as the Geiger counter.
- [7] E. Storm, H. I. Israel, *At. Data Nucl. Data Tables* **1970**, *7*, 565–681.
- [8] M. J. Bowden, J. H. O'Donnell in *Developments in Polymer Degradation*, Vol. 6, Elsevier, Barking, **1985**, pp. 21–61.
- [9] J. R. Brown, J. H. O'Donnell, *Macromolecules* **1972**, *5*, 109–114.
- [10] a) M. J. Bowden, L. F. Thompson, *J. Appl. Polym. Sci.* **1973**, *17*, 3211–3221; b) T. R. Pampalone, *J. Imaging Sci.* **1986**, *30*, 160–166; c) N. Yao, Z. L. Wang in *Handbook of Microscopy for Nanotechnology*, Kluwer, Boston, **2005**, pp. 287–319.
- [11] P. B. Ayscough, K. J. Ivin, J. H. O'Donnell, *Trans. Faraday Soc.* **1965**, *61*, 1110–1117.
- [12] T. N. Bowmer, J. H. O'Donnell, *J. Macromol. Sci. Part A* **1982**, *17*, 243–263.
- [13] A. H. Fawcett in *Encyclopedia of Polymer Science & Engineering*, Vol. 10, Wiley-VCH, Weinheim, **1987**, pp. 408–432.
- [14] Numerous examples for post-polymerization modification of other families of polymers have been described in the literature. For a look at the scope of examples on click chemistry for post-polymerization modification and main chain polymerization, see *Macromolecules* **2009**, virtual issue, issue 1.
- [15] R. J. Chen, Y. Zhang, D. Wang, H. Dai, *J. Am. Chem. Soc.* **2001**, *123*, 3838–3839.
- [16] H. Paloniemi, T. Ääritalo, T. Laiho, H. Liuke, N. Kocharova, K. Haapakka, F. Terzi, R. Seeber, J. Lukkari, *J. Phys. Chem. B* **2005**, *109*, 8634–8642.

- [17] Even though it has traditionally been considered that ^{209}Bi was the heaviest stable isotope in the periodic table, it was actually shown that the half-life is just extremely long (1.9×10^{19} years). However, this supposition can be considered correct for our system. P. De Marcillac, N. Coron, G. Dambier, J. Leblanc, J.-P. Moalic, *Nature* **2003**, 422, 876–878.
- [18] H. Tamber, J. Smid, I. Cabasso, *Chem. Mater.* **1997**, 9, 1335–1341.
- [19] rad = radiation absorbed dose. $1 \text{ rad} = 1 \text{ cJ kg}^{-1} = 1 \text{ cGy}$.
- [20] Comparable organic-based small-size solid state systems in which the sensing mechanism relies on other phenomena present the following detection limits: Scintillation of conjugated polymers: a) $> 10^5 \text{ rad}$ (undoped system), E. A. B. Silva, J. F. Borin, P. Nicolucci, C. F. O. Graeff, T. Ghilardi Netto, R. F. Bianchi, *Appl. Phys. Lett.* **2005**, 86, 131902; b) $0.5 \times 10^3 \text{ rad}$ (doped system), Y. S. Zhao, H. Zhong, Q. Pei, *Phys. Chem. Chem. Phys.* **2008**, 10, 1848–1851; Charge generation in organic semiconductors: $4.1 \times 10^6 \text{ rad}$, H. N. Raval, S. P. Tiwari, R. R. Navan, V. R. Rao, *Appl. Phys. Lett.* **2009**, 94, 123304.
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