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Reduction of radiation-induced conductivity in poly(ethylene terephthalate): Effect of dopant structure

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ABSTRACT

This paper focuses on developing radiation tolerant polymeric films by incorporating small molecule dopants into the material formulation. The radiation tolerance is imparted to the polymer by dopants capturing the mobile electrons generated upon radiation exposure. A wide range of conjugated small molecules was utilized for the reduction of radiation-induced conductivity (RIC) in semi-crystalline poly(ethylene terephthalate). Using these results, the process of electron and hole trapping by π-conjugated molecules may be generalized to many organic systems. All conjugated ring cores examined, when substituted with an appropriate electron-withdrawing species, led to excellent RIC reduction. The nitro group is the strongest electron-withdrawing substituent, and therefore leads to the lowest RIC, but other substituents also reduce RIC, and the interactions may be quantified by the Hammett parameter. It was also found that the dopant must be present in a certain range of concentrations, between 10 and 200 mol/m^3 (6×10^{18} and 1×10^{20} molecules/cm^3), for proper trapping of the photo-induced electron-hole pairs. This understanding of the interactions between conjugated dopants, photons, and electrons will benefit other applications, such as controlled conductivity in coatings and organic electronics.

1. Introduction

The placement of π-conjugated dopants into organic materials with the proper dopant chemistry and concentration can impart unique optical and electronic properties to the material, due to the ability of the dopant to interact with the electrons, holes, or photons. Although recent developments in the fields of solid-state lighting, radio frequency identification tags, and solar cells have garnered significant scientific attention [1,2], implementation of π-conjugated dopants can also enable novel technologies for space and sensor applications. Polymeric dielectrics, when exposed to ionizing radiation, undergo the formation of mobile electron–hole pairs, leading to radiation-induced conductivity (RIC) [3]. Ionizing radiation may consist of X-rays, γ-rays, protons, or high-energy electrons. The incorporation of conjugated structures possessing the proper chemistry will reduce the RIC dramatically by trapping the mobile electrons or holes. Although typically only experienced in extreme environments, the behavior of ionizing radiation and the resulting electron-hole pairs in organic materials are equivalent to that in organic semiconductors, and this behavior is also relevant to additional applications such as the enhancement of breakdown strength or the reduction of conductivity at interfaces using selective coatings.

RIC severely limits the insulating capability of these dielectrics in ionizing-radiation environments, and is especially crippling to applications such as energy storage materials, protective coatings, underfills, and encapsulants. One effective method to reduce RIC is to include deep energy wells within the polymer to trap the predominantly conductive carriers (either electrons or holes, depending on the polymer), thereby limiting the mobility of these carriers through the material. However, high-quality polymeric dielectrics with sufficient radiation tolerance are not widely commercially available, and therefore a process of doping films with electron traps has been developed. This was first demonstrated as an effective approach by implanting small molecules of 2,7,9-trinitrofluorenone in DuPont Mylar® C capacitor-grade film [3]. Further research has demonstrated this approach for several other dopants [4]. The creation of electrons and holes with incident radiation and the consequent trapping of electrons (and potentially

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the pinning of holes) by small molecule traps follows a complex series of mechanisms that vary depending on the polymer and dopant [6–8]. However, the key principle of reducing RIC by implanting small molecule electron traps works for a variety of small molecules provided the trap is of sufficiently deep energy. This paper investigates the functionality required to obtain the sufficient trap energy depth and thereby instill radiation tolerance.

2. Experimental

For this work, the following chemicals were obtained from Sigma–Aldrich (S–A) or Fisher Scientific (F) unless otherwise noted: 2-Nitrofluorenone (99%, S–A), 2,7-dinitro-9-fluorenone (97%, S–A), 2,5-dinitro-9-fluorenone (90%, S–A), 2,5,7-trinitro-9-fluorenone (99%, Sandia National Laboratories), 4-cyano-9-fluoronone (99.5%, F), 1-aminopyrene (97%, F), 1-nitropyrene (99%, F), 1,3,6-trinitropyrene (90%, S–A), 1,3,6,8-tetranitropyrene (90%, S–A), 9,10-dinitroacenaphthene (90%, S–A), 1-aminoanthracene (90%, S–A), 9-nitroanthracene (95%, S–A), isopropanol (99.9%, F), acetone (99.7%, F), toluene (99.9%, F), and ethylene glycol (electronic grade, Air Products). Mylar® C capacitor grade poly(ethylene terephthalate) film 12.9 μm thick was obtained from DuPont. Chemical structures of the dopants and polymer are given in Fig. 1. Specific positions around the unsaturated cores are as following. For the fluorenones: nitrofluorenone (NF) 1 = nitro; 2,7-dinitrofluorenone (DNF) 1,2 = nitro; 2,5-dinitrofluorenone (DNF) 1,3 = nitro; trinitrofluorenone (TNF) 1,2,3 = nitro; and cyanofluorenone (CF) 3 = cyano. For the pyrenes: aminopyrene (AP) 1 = amino; nitropyrene (NP) 1 = nitro; trinitropyrene (TNP) 1,2,3 = nitro; and tetranitropyrene (TetNP) 1,2,3,4 = nitro. For the acenaphthenes: nitroacenaphthene (NAc) 1 = nitro. For the anthracenes: nitroanthracene (NAnt) 1 = nitro.

Prior to doping, Mylar® films were first wiped with a cloth soaked in isopropanol to clean the surface. Doped films were then prepared by immersing films in baths of heated EG solutions of desired concentrations of small molecule dopants for specified times. Solution temperature T and solution concentration C_S were carefully controlled over the duration of the doping time t. The doped films were then removed and rinsed in isopropanol, acetone, and toluene to remove excess dopant and EG from the surface, followed by annealing under vacuum at 82 °C, the Mylar® T_g, for at least 12 h. In order to measure average concentration for each dopant, concentration calibration curves were established by ultraviolet–visible (UV–vis) spectroscopy (Perkin–Elmer Lambda 950) in transmission mode using solutions of known concentrations. Analysis of the UV–vis spectra was described in a previous publication by Lenhart et al. [4]. Electrodes were evaporated on the film surfaces to form a simple capacitor, wires were attached, and the film was potted in epoxy to prepare for RIC exposure (described in detail by Lenhart et al. [4]). Two conditions were evaluated during exposure to a constant 30 rad/s (Si) dose rate of incident radiation: zero applied voltage and 29 V/μm. The total radiation-induced current over time was obtained by subtracting the background current (obtained at zero applied voltage) from that measured during radiation exposure. Note that a wait time, between the application or removal of voltage and the measurement of RIC, allowed for the dielectric relaxations of the Mylar® to reach steady state.

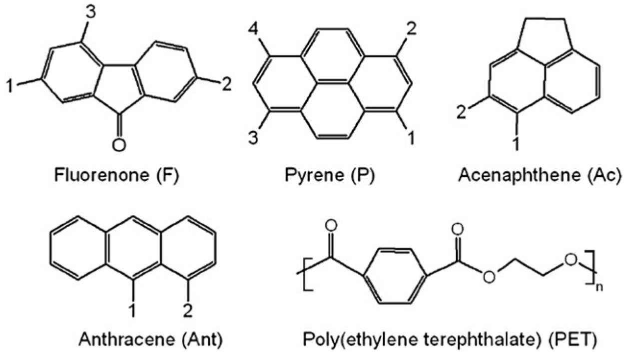

Fig. 1. Chemical structures of the dopants and polymer used in this study. The numbered positions on the dopants indicate the potential positions of functional groups (nitro, amino, or cyano groups), as specified in the text.

3. Results and discussion

Representative RIC response curves are shown in Fig. 2: both undoped Mylar® and NF-doped Mylar® exhibit the same basic rise to a plateau under exposure to constant radiation. The baseline response, generated under zero applied voltage and 30 rad/s (Si), is slightly negative, likely due to the effect of the radiation on the connecting wires and surrounding epoxy. The average radiation-induced current is evaluated as the magnitude of the corrected plateau after baseline subtraction, and is averaged over two to four separate runs.

The first critical result obtained from testing a variety of dopants is that dopant concentration has an important effect on RIC. This was first observed by Kurtz et al. [9], who roughly noted that 50 mol/m^3 TNF in Mylar® results in a lower RIC than either 6 mol/m^3 on the low end or 200 mol/m^3 on the high end (1.0 mol/m^3 = 6.0×10^{17} molecules/cm^3). If the dopant concentration is too low, there are insufficient molecules to trap the radiation-induced electrons; and if the concentration is too high, electrons can percolate through the matrix by tunneling between small molecules [9,10]. The rise in RIC at high concentrations begins near 200 mol/m^3 or 1×10^{20} molecules/cm^3, which by the present method of doping is difficult to reach so the primary concern for deviations from the plateau is at low concentrations. Fig. 3 provides radiation-induced current as a function of concentration for NF and DNF: above 10 mol/m^3, the current settles at a plateau, and this behavior is consistent across all dopants tested. In addition, comparison of 2,5-DNF to 2,7-DNF indicates that the positions of the nitro groups in DNF do not impact the RIC behavior. Generalizing this concept, it

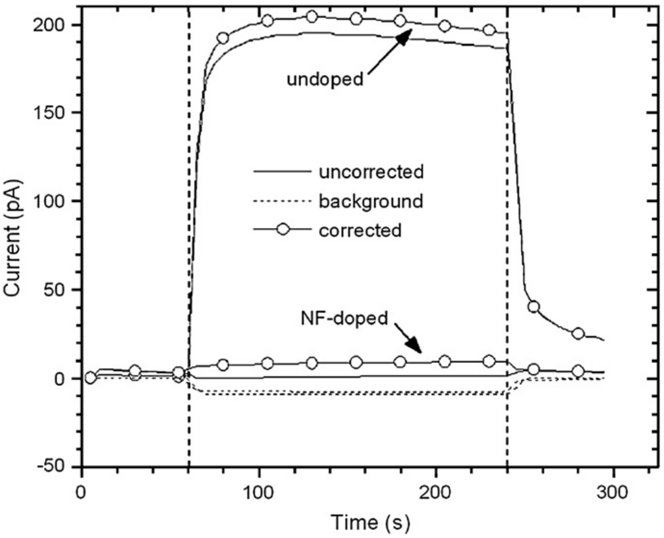

Fig. 2. RIC as a function of time for undoped Mylar® and Mylar® doped with NF at 21 mol/m^3. Uncorrected data indicate the RIC measured at 29 V/μm, and background data indicate the RIC measured with no voltage applied; the corrected data are the latter subtracted from the former. Vertical dashed lines indicate when exposure to 30 rad/s (Si) began and ended.

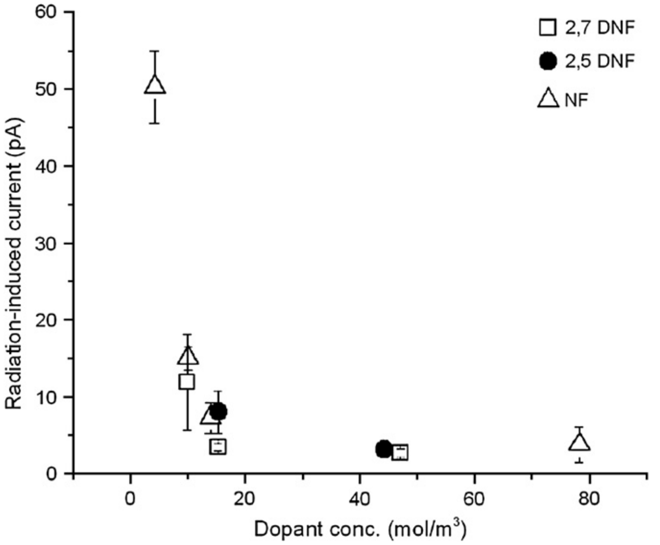

Fig. 3. RIC under 30 rad/s (Si) and 29 V/μm as a function of dopant concentration for NF, 2,7-DNF, and 2,5-DNF.

is the presence of electron-withdrawing substituents, not the position on the ring, that leads to deep electron traps.

Having established the minimum dopant concentration for reliable RIC measurements, we can examine RIC across a broad range of dopants without being concerned about large variations in RIC with dopant concentration. Several trends immediately emerge from inspection of Fig. 4. First, all four dopant types – fluorenones, pyrenes, acenaphthenes, and anthracenes – resulted in excellent RIC reduction when modified with one or more nitro substituents. This demonstrates the universality of imparting RIC tolerance: any conjugated ring core attached to a strong electron-withdrawing substituent confers excellent RIC tolerance to Mylar®, provided the dopant concentration is in the optimal range.

Second, the addition of a cyano substituent is also effective at reducing RIC, although not as effective as a nitro substituent, due to the weaker electron-withdrawing ability of the cyano group. Interestingly, conjugated ring cores with no pendant functionality still impart modest radiation tolerance (∼25% RIC reduction). Also, the addition of an amino substituent, an electron-donating species, to the conjugated ring cores reduces RIC by ∼50%. These observations can be analyzed in a semi-quantitative way by comparison with the Hammett parameter. The Hammett parameter is an empirical electronic substituent parameter that is determined by the ability of a substituent to enhance the acidity of substituted benzoic acid relative to unsubstituted benzoic acid [11]. Positive values for σ indicate electron-withdrawing; negative values indicate electron-donating. While several other classes of σ values have been defined via additional chemical reactions [11], this discussion selects σ derived from benzoic acid due to the similarities between the benzene ring in benzoic acid and the conjugated rings in the cores of the dopants under consideration. The main inconsistency in using Hammett parameters to predict electron-trapping ability is that the values for σ differ according to their location on the ring (indicating a localized effect), whereas the depth of an electron trap may not vary with the position of the electron-withdrawing substituent, as illustrated in Fig. 2.

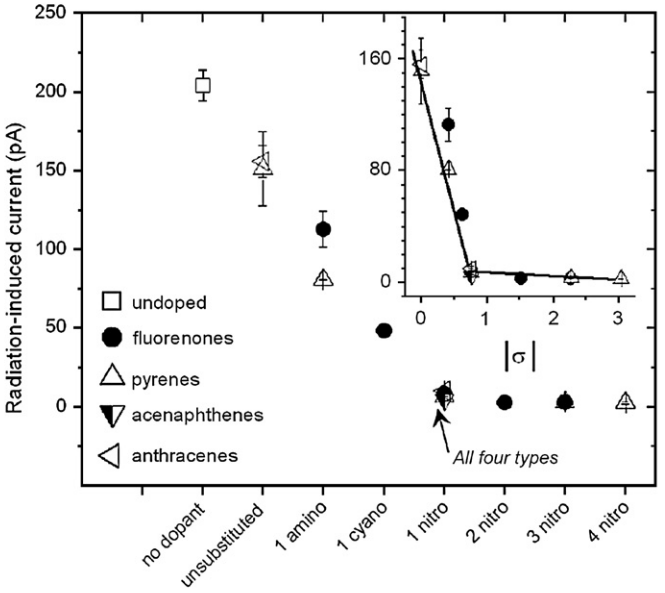

Fig. 4. RIC while exposed to 30 rad/s (Si) and 29 V/μm for all available data. The primary horizontal axis is arbitrarily spaced, whereas the inset is plotted as a function of absolute Hammett parameter σ, averaged over *meta* and *para* values (Table 1).

Table 1
Hammett parameters [10] for the nitro, cyano, and amino substituents, when located at the *para* or *meta* position of benzoic acid

Substituent	σ_{para}	σ_{meta}
$-NO_2$	0.77	0.74
–C≡N	0.65	0.61
$-NH_2$	−0.63	−0.21
–H	0	0

Parameters are dimensionless due to normalization by the acidity constant of unsubstituted benzoic acid.

Among the four substituents in Table 1, the nitro group is the most electron-withdrawing, followed by the cyano group. The amino group is actually electron-donating, surprising when considered alongside the beneficial impact to RIC reduction in the amino-substituted molecules under consideration. Prior investigations of Mylar® have illustrated that mobile electrons are the dominant cause of RIC and that holes contribute negligibly [12]. This explanation fits well with our observations of substantial RIC reductions upon doping with aromatic cores substituted with pendant electron-withdrawing species. However, other studies have presented contradictory results where hole mobility contributed substantially to RIC in Mylar® [13]. Given the result here that an electron-donating substituent (amino) on the conjugated ring reduces RIC over the unsubstituted species, it is tempting to conclude that hole traps can be nearly as effective as electron traps. More research is warranted to distinguish between the effectiveness of electron and hole trapping; at this point, we assert that all pendant substituents in question increase electron-withdrawing capability of the trap. However, it is certain that rings substituted with electron-withdrawing species are stronger electron traps than those unsubstituted or substituted with electron-donating species.

We quantify the dependence of the RIC reduction on the substituent Hammett parameter in the inset of Fig. 4, using the absolute value of the Hammett parameter (averaged over *meta* and *para* values). A roughly linear reduction is observed down to small values of RIC, whereupon additional substituents have little further effect. Although quantification by the Hammett parameter is not completely rigorous due to the reasons given above, this correlation can enable predictions of the RIC-reducing ability of other dopants with minimal experimental verification.

4. Summary

In summary, guidelines for RIC reduction by doping polymeric dielectrics with an effective electron trap have been established. Dopants should be present in concentrations between 10 and

200 mol/m^3 (6×10^{18} and 1×10^{20} molecules/cm^3). The most effective small molecule dopants contain a conjugated ring core with an electron-withdrawing substituent such as a nitro or cyano group. All of the conjugated ring cores examined – fluorenones, pyrenes, acenaphthenes, and anthracenes – performed extremely well when substituted with a nitro group, and it is expected that the list can be extended to many additional conjugated ring structures. Other substituents may also be effective, and the effectiveness of a particular dopant may be semi-quantitatively predicted using the Hammett parameter. With a strong electron-withdrawing substituent pendant to the ring, the position of the pendant group had no apparent impact. These results are not only relevant to RIC reduction: the ability to trap electrons in organic films may have additional applications such as the enhancement of breakdown strength, optimization of organic electronic materials, or the reduction of conductivity at interfaces using selective coatings.

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References

[1] Coropceanu V, Cornil J, da Silva Filho DA, Olivier Y, Silbey R, Bredas JL. Chemical Reviews 2007;107(4):926–52.

[2] Walzer K, Maennig B, Pfeiffer M, Leo K. Chemical Reviews 2007;107(4): 1233–71.

[3] Kurtz SR, Arnold C, Hughes RC. Applied Physics Letters 1983;43(12):1132–4.

[4] Lenhart JL, Cole PJ, Schroeder JL, Lacy SM, Belcher M. Journal of Applied Physics 2008;103(2):024908.

[6] Hughes RC. Journal of Chemical Physics 1973;58(6):2212–9.

[7] Khatipov SA. High Energy Chemistry 2001;35(5):291–307.

[8] Tyutnev AP, Saenko VS, Smirnov IA, Pozhidaev ED. High Energy Chemistry 2006;40(5):319–30.

[9] Kurtz SR, Arnold C, Hughes RC. IEEE Transactions on Nuclear Science 1983; 30(6):4077–80.

[10] Gill WD. In: Garmish-Partenkirchen, editor. Proceedings of the 5th international conference on amorphous and liquid semiconductors. London: Taylor and Francis; 1973. p. 901.

[11] Pross A. Theoretical and physical principles of organic reactivity. New York: John Wiley and Sons, Inc; 1995. p. 159–82.

[12] Kurtz SR, Arnold JC. Journal of Applied Physics 1985;57(7):2532–7.

[13] Hayashi K, Yoshino K, Inuishi Y. Japanese Journal of Applied Physics 1975; 14(1):39–45.